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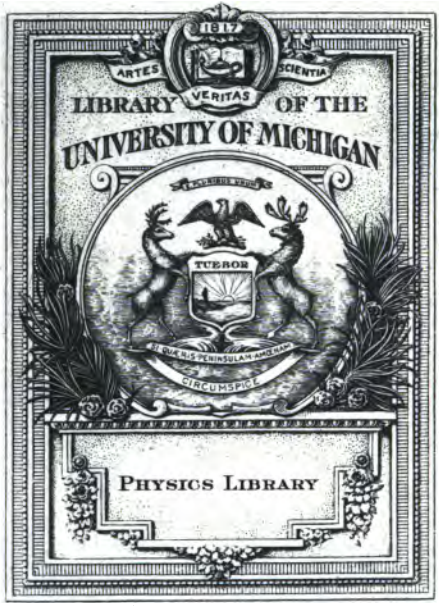
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HEAT
FOR ADVANCED STUDENTS

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HEAT

FOR ADVANCED STUDENTS

BY

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PREFACE

MY aim in writing this book has been to give a comprehensive account of the science of Heat in both its theoretical and experimental aspects, so far as this can be done without the use of the higher mathematics. It is intended for students who already possess an elementary knowledge of fundamental physical principles, but whose training has not, as yet, qualified them to derive full benefit from more advanced text-books, foremost amongst which must be placed the excellent treatise on "The Theory of Heat," by Professor Thos. Preston, M.A., F.R.S., &c.

Much recent work has been included in order to give as complete and many-sided a survey of the subject as possible. The experiments to be performed by the student have been selected so as to illustrate the most important points in each chapter, and it is believed that the descriptions given will be found sufficient to ensure accurate results.

Great stress has been laid on the necessity for due precautions in connection with thermometry. The whole science of heat is based on thermometric measurements, hence too great an importance cannot be attached to this part of the subject.

Following the nomenclature used in the *Smithsonian Physical Tables*, the term *therm* has been used to denote the quantity of heat necessary to raise the temperature of one gram of water through 1° C. Confusion between the *gram-calorie* and the *kilogram-calorie* (which are often indiscriminately denoted by the term calorie) is thus avoided.

In treating of Thermodynamics an acquaintance with the method of expansion by the Binomial Theorem is assumed.

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The notation of the infinitesimal calculus has been used, but each problem has been worked out from first principles, no previous knowledge of the calculus being taken for granted. The proofs given are consequently often much longer than those found in advanced text-books, but the clear indication of the various assumptions made in the course of each investigation will prove a sufficient compensation to the conscientious student. The necessity for a careful study of Thermodynamics has been emphasised by the recent publication of popular accounts of the "wonderful" properties of liquid air. Even a slight knowledge of thermodynamical principles would have created as much distrust in these reports as in an account of any other method of obtaining perpetual motion.

A short section has been devoted to the use of Temperature-Entropy diagrams.

Owing to the kindness of the publishers a considerable number of illustrations, representing historic apparatus, has been included, those marked [P.] being from the previously mentioned treatise of Prof. Preston, but no fewer than 155 figures have been specially prepared for the book.

My best thanks are due to Prof. R. A. Gregory and Mr. A. T. Simmons for their constant help and advice whilst the sheets have been passing through the press. Mr. Robert B. Thompson and Mr. Leslie H. Hounsfield have also kindly read the proofs of the earlier pages, and their criticisms, being those of earnest and painstaking students, have proved most valuable.

My thanks are also due to the authorities of the Albert and Victoria Museum, South Kensington, who kindly gave me permission to photograph some valuable historical apparatus in their collections for reproduction in this book.

EDWIN EDSER.

PUTNEY,
September, 1899.

The attention of students is directed to the solutions of difficult problems given on pp. 473–487.

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HEAT
FOR ADVANCED STUDENTS

CHAPTER I

TEMPERATURE AND THERMOMETRY

Temperature.—Our unaided senses suffice to distinguish between those conditions of a body which are designated by the terms *hot* and *cold*. It may, however, be remarked that the information thus acquired is of a somewhat relative character. A well-known experiment will illustrate this.

EXPT. 1.—Arrange three bowls, A, B, C, so that A contains cold water, B contains water that is somewhat warmer than that in A, whilst the water in C is warmer than that in either A or B. Immerse the right hand for some time in C, the left hand at the same time being immersed in A. Now plunge both hands into B; the water in this bowl will be felt to be cold by the right, and warm by the left hand.

On a frosty day, a piece of metal which has been exposed to the air, will seem colder, when touched, than a piece of wood which has been similarly treated, although both the wood and metal are really equally cold.

Nevertheless, our ideas of hotness and coldness are fundamentally derived from our sensations; and though we may have cause to distrust, in particular instances such as those given above, the information which we obtain through these channels, it does not follow that we should, even were it possible, discard entirely these foundations for our knowledge of the phenomena connected with the science of Heat.

We may understand the expression "the temperature of a body" to mean its hotness (in the first place as determined by our sensations), compared with some standard temperature to be selected. A satisfactory definition of the meaning of the term "temperature" is at present impossible; the definitions which have been proposed either contain vague terms which render their use exceedingly unscientific, or else they define a state, of which we have some positive knowledge, in terms of certain assumptions which are really forced upon us by phenomena connected with the very condition which we seek to define. The latter form of arguing in a circle is to be particularly discountenanced.

Unsatisfactory Definitions of Temperature.—A few remarks upon some definitions[1] of temperature, frequently met with, but fundamentally unsatisfactory, will illustrate the difficulty of expressing the meaning of temperature in exact words.

1. "The temperature of a body is the energy with which the heat in a body acts in the way of transferring or communicating a portion of itself to other bodies."

This is a mere string of words, which may be learnt by heart, and may so give a feeling of knowledge gained. But upon analysis it is found to explain temperature—of which, as before remarked, we have some definite knowledge—in terms of "heat" (a hypothetical substance) and "energy" (a term which has a definite mechanical signification, but is here loosely applied, or misapplied).

2. "The temperature of a body is its power to communicate heat to other bodies."

This definition, though simple, and therefore to be preferred to the above, is essentially bad: (*a*) in the use of the term "power" in an unscientific sense, and (*b*) in introducing the assumption of something new and unknown, termed "heat," to explain temperature.

Other similar definitions comprise such terms as "sensible heat." These are either unmeaning or erroneous. We are not directly sensible of heat, but of the temperature to which our skin is raised.

At this stage, therefore, we may much more usefully understand by *temperature* merely *the hotness of a body measured in a manner to be subsequently agreed upon.*

---

[1] For a further discussion of this point see Preston's *Heat*, p. 31. Macmillan and Co.

A great part of the science of Heat is occupied with settling the most trustworthy methods of measuring temperature. Some of these methods will be described in the present chapter.

Thermoscopes.—A thermoscope may be defined as an arrangement which indicates the attainment of a certain arbitrary temperature.

EXPT. 2.—Support a piece of thick sheet copper in a horizontal position on a tripod stand, and sprinkle small quantities of sulphur, lead, washing soda, paraffin wax, sealing wax, &c., &c., on it; then, if the copper be gradually heated by means of a Bunsen burner, it will be found that first one and then another of these substances will be melted.

We might, therefore, when the paraffin wax melts in the foregoing experiment, say that the copper is at the temperature of melting paraffin wax, and so on. This method is actually used in certain scientific experiments.

EXPT. 3.—It is well known that the dimensions of almost all bodies are altered by a change of temperature. A well-known experiment illustrates this. A brass ball which, when cold, will pass freely through a certain circular aperture, is found to be too large to do so when its temperature has been considerably raised. On cooling, however, it falls through the aperture when a certain temperature is reached, and we might use this fact to define a certain arbitrary temperature of the ball.

A Thermometer is an Instrument designed to measure Temperature.—As a matter of fact, thermometers primarily indicate the temperature of the substances employed in their construction; but it is generally arranged that these substances should acquire the temperature of the medium in which they are placed.

Any property of matter which varies continuously with the temperature might be used to measure temperature. Thus, linear expansion, cubical expansion or dilatation, the electrical resistance of a conductor, the thermo-electric force at the junction of the two unlike metals—all these and many other properties are used to measure temperature. In every case, however, the measurements are based on the arbitrary selection of two standard temperatures, and the subdivision of the interval between them into a convenient number of divisions or degrees.

The methods used in measuring temperature, and the precautions to be adopted in constructing a thermometer, are well illustrated in the construction and use of a mercury thermometer, which will now be described.

Mercury Thermometer.—When mercury is heated, its volume increases ; consequently, if a method of measuring this increase of volume can be arranged, the temperatures corresponding to any given increase can be defined.

Let us suppose that we have a bulb blown on the end of a glass tube, and that the bulb and part of the tube are filled with mercury. Let us further assume, for the moment, that the volume of the bulb and tube remains unaltered as the temperature is varied. Then, if the mercury be cooled to the temperature of melting ice, by immersing the bulb and the part of the stem filled with mercury in ice-shavings or snow, the position occupied by the mercury meniscus may be marked on the stem, thus giving one fixed temperature.

It is known that a pure liquid boils at a constant temperature as long as the pressure of its vapour is maintained constant. Consequently, the temperature of the vapour above pure water, boiling under some arbitrary pressure, will be constant, and we may define this as the second fixed point on the thermometric scale. The bulb and that part of the tube containing mercury are placed in steam, and the position of the extremity of the mercury column is marked on the stem.

FIG. 1.—Mercury Thermometer.

If the bore of the tube is uniform along its whole length, then we may divide the space between these two marks into any convenient number of equal spaces—one hundred such spaces are marked on an ordinary

Centigrade thermometer. When the mercury meniscus is opposite any one of these, we may state that the temperature of the mercury has a certain value; and if the conditions of the experiment are so arranged that the thermometer thus constructed has had an opportunity of acquiring the temperature of the surrounding medium, we may thus determine the temperature of the latter.

We have tacitly assumed, up to the present, that one end of the thermometer tube is open to the atmosphere. The disadvantages of this arrangement are:

1. Liquids or foreign substances might enter the tube, and thus cause trouble.

2. Mercury might leave the tube; this would certainly happen, since mercury slowly evaporates, even at ordinary temperatures.

Consequently, an advantage will be gained by closing the end of the tube. As a general rule, the space above the mercury is freed from air; if this were not so, the pressure produced by the compression of the enclosed air by the expanding mercury would break the walls of the bulb, unless these were very thick.

Construction of a Thermometer.—The first thing to be attended to in this connection, is the selection of the tube to be used for the stem of the instrument. As to the bore of the tube, it can easily be seen that the smaller this is, the greater will be the sensitiveness of the thermometer, assuming the bulb to have the same size in all cases; or, on the other hand, for a given sensitiveness, the size of the bulb can be diminished, according as a tube of a finer bore is employed. The exact relation between the bore and the size of the bulb may be determined as follows:—

Let v = volume of bulb. (If the bulb is spherical, $v = \frac{4}{3}\pi R^3$, where R = radius of the sphere.)

Let a = internal sectional area of tube. (If the section of the bore is circular, $a = \pi r^2$, where r = internal radius of the tube.)

Let x = distance that the end of the thread of mercury in the stem moves through for a rise of temperature of 1° C.

Let α = the increase in volume experienced by unit volume of mercury when heated through 1° C.

The increase in the volume of the mercury contained by the bulb when the temperature is raised by 1° C = $v\alpha$. This mercury flows into the stem, and fills an extra length x of the latter.

$$\therefore ax = v\alpha \therefore x = \frac{v\alpha}{a}.$$

With a spherical bulb and a stem of circular bore,

$$x = \frac{\frac{4}{3}\pi R^3}{\pi r^2}\alpha = \frac{4}{3}\frac{R^3}{r^2}\alpha.$$

EXAMPLE.—It is required to construct a mercury thermometer from tubing of circular bore, the internal diameter being equal to ·2 mm. What must be the diameter of the bulb blown (taking α = ·000181 per 1° C.) in order that the distance between consecutive degree divisions should be equal to 2 mm.?

In accordance with the above reasoning $R^3 = \frac{3}{4}\frac{xr^2}{\alpha}$.

$$\therefore R^3 = \frac{3}{4} \times 2 \times (\cdot 1)^2 \times \frac{1}{\cdot 000181} = 82\cdot 8.$$

$$R = \sqrt[3]{82\cdot 8} = 4\cdot 36 \text{ mm.}$$

∴ Internal diameter of thermometer bulb = 8·72 mm.

This example shows that in order to obtain reasonable sensitiveness, combined with a bulb of moderate size, a tube of very small bore must be used.

Thermometers with Cylindrical Bulbs.—Ordinary chemical thermometers are made with cylindrical bulbs, so as to facilitate their introduction into flasks, &c., through small apertures. A not uncommon length for such a bulb would be 20 mm., the diameter being about 3 mm. Let us now determine what must be the diameter of the tube employed, in order that successive degree divisions should be 2 mm. apart.

$$x = 2 \text{ mm.}$$
$$v = \pi \times (1\cdot 5)^2 \times 20 \text{ c. mm.}$$

Hence, if r = internal radius of the tube employed, which is supposed to have a circular bore,

$$\pi r^2 \times 2 = \pi \times (1\cdot 5)^2 \times 20 \times \cdot 000181.$$
$$r^2 = \cdot 0040689 \text{ mm.}$$
$$r = \cdot 0637 \text{ mm.}$$

∴ Internal diameter of tube = 0·1274 mm.

This bore is so small that great difficulty would be experienced in noting the position of the end of the mercury thread. In order to overcome this difficulty, tubing with an elliptical or flattened bore (Fig. 3) is generally used. Thus, when the mercury is viewed at right angles to the longer axis of the ellipse, the position of the end of the column is plainly visible. The glass itself serves to furnish a magnified image of the mercury column. In addition, a layer of white enamel is frequently embedded at the back of the tube; thus giving a good background for viewing the mercury.

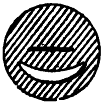

FIG. 3.—Section of Stem of Chemical Thermometer.

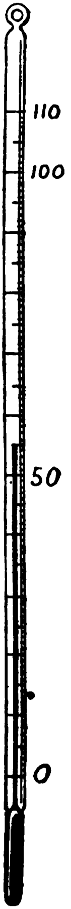

FIG. 2.—Chemical Thermometer.

In chemical thermometers of the class under discussion, the graduations are generally engraved on the front or clear glass surface of the thermometer tube. In taking readings, it is necessary to carefully avoid parallax. This can be done with great accuracy by placing the eye in such a position that the engraved divisions in the neighbourhood of the top of the mercury column are seen just to overlap their reflections in the mercury.

Thermometer Tubes should be of Uniform Bore.—In selecting a tube for the construction of a thermometer, it is most important to determine whether the bore is uniform throughout the length to be used. This point may be settled by carefully sucking a short thread of mercury into the tube, and measuring its length when occupying various positions in it. A tube in which these lengths vary by more than a very small amount should be discarded.

The bulb of the thermometer is sometimes blown directly from the glass composing the tube, but more often is made independently and fused on to the stem. Before doing so, the inside of the tube is carefully cleaned, as any traces of dust or other foreign matter will subsequently cause great trouble and annoyance.

Filling the Thermometer.—Before the bulb has been sealed on to one end of the stem, a thistle funnel A is blown on the other end of the latter. The tube is also drawn out at the point B where the thermometer is to be sealed off. In doing this, care must be taken to pull the tube out as little as possible, but to allow the glass to collapse so as to leave only a very fine aperture, the walls remaining thick.

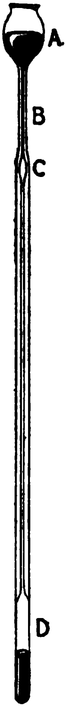

Fig. 4.—Chemical Thermometer in Course of Construction.

It is further worth while to blow a small expansion, C, at a point just above the position selected for the graduation marking the highest temperature which the thermometer is required to measure. By this means accidental breakage of the thermometer through a small overheating is guarded against.

The funnel A having been filled with pure dry mercury, the bulb D is slightly heated so as to drive out some of the imprisoned air. On allowing D to cool, mercury will be drawn in. Amateurs often heat the bulb too much to start with, resulting in a breakage due to the cold mercury suddenly cooling the hot glass. When once a small amount of mercury has been drawn into the bulb there is less fear of this mishap, since the bulb is then not likely to be heated to a greater temperature than that of boiling mercury.

Subsequent heatings and coolings will suffice to entirely fill the bulb and stem with mercury. Finally the whole of the contained mercury must be boiled. This cannot be done without considerable risk when nothing further than a naked flame is used. Greater safety is attained by placing the thermometer, together with its attached thistle funnel filled with mercury, in an enclosure which can be heated to a sufficiently high temperature, and subsequently allowed to cool gradually. The mercury is boiled in order to drive off the air which otherwise always clings to the walls of the tube.

In order to seal the thermometer off, the mercury in the bulb and stem is raised to a temperature sufficiently above that which is to correspond to the highest graduation ; this temperature will be that at which the thermometer will burst after being sealed off. A small pointed flame is then directed on to the constriction B, Fig. 4, and the mercury having been evaporated from the neighbourhood of the point of the flame, the temperature is increased till the tube fuses and the walls fall together, when the upper part may be pulled off.

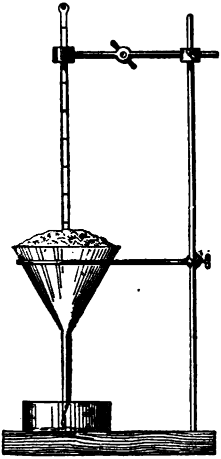

FIG. 5.—Arrangement for Determining the Freezing Point of a Thermometer.

Determination of the Fixed Points.—The determination of the fixed points of a thermometer should be postponed for at least a week after the thermometer has been filled and sealed. The most convenient fixed points for a thermometric scale are those corresponding to the melting of pure ice in distilled water, and the boiling point of water at standard atmospheric pressure.

In order to determine the freezing point, the lower part of the thermometer is surrounded with ice shavings, or freshly-fallen snow ; a better result is thus obtained than when ice in the form of small blocks is used. For a very accurate determination, distilled water contained in a test tube is frozen round a piece of copper rod, and the latter having been removed, the thermometer bulb is placed in the aperture so formed, the space between the bulb and the ice being filled with distilled water. The whole is then placed in an inverted funnel filled with ice shavings, and left for a space of half an hour or so. The position of the extremity of the mercury column may then be marked, and if it is found that no alteration in its position takes place in about ten minutes, this point may be taken as the freezing point, or zero of the thermometer.

In order to facilitate marking the position of the freezing point, a thin layer of varnish or paraffin wax may be laid on the stem; a scratch in this may be subsequently etched into the glass by means of hydrofluoric acid gas.

EXPT. 4.—You are provided with a mercury thermometer, a funnel, some ice, and a chisel or a steel plane, and are required to test the accuracy of the freezing point (0° C.) as marked on the thermometer.

By means of the chisel or plane obtain a quantity of ice shavings and place these in the funnel. Embed the thermometer bulb and the lower part of the tube in these, and take readings at intervals, entering these in your observation book. The reading which the mercury meniscus finally gives may be taken as the true zero of the thermometer. Hence deduce the error of the instrument supplied, and write this down, being careful to note whether this error is + or −.

The correct determination of the boiling point of a thermometer is a matter of greater difficulty. It is best to mark the position of the extremity of the mercury column when the bulb and stem are surrounded by steam, at the same time noting the height of the barometer. A correction can then be calculated, giving the amount by which the graduation so obtained is removed from the boiling point under standard atmospheric pressure.

The apparatus used for the determination of the boiling point is shown in Fig. 6. It is best to provide the cork, through which the thermometer is thrust, with a rather large hole, the thermometer being prevented from slipping through by a ring cut from a piece of indiarubber tubing fitting tightly on it. The whole of the stem as far up as the extremity of the mercury column should be surrounded by steam. When the extremity of the mercury column has attained a position which does not alter during five or ten minutes, it can be marked by a scratch, and the barometer immediately read.

The thermometer tube may now be graduated. A coat of paraffin wax having been laid evenly over the stem, the distance between the fixed points is divided into 100 equal parts (200 parts if half degree graduations are employed). The positions of the graduations are marked by scratches in the wax. They may be etched into the glass by hydrofluoric acid, the vapour being used in preference to the liquid.

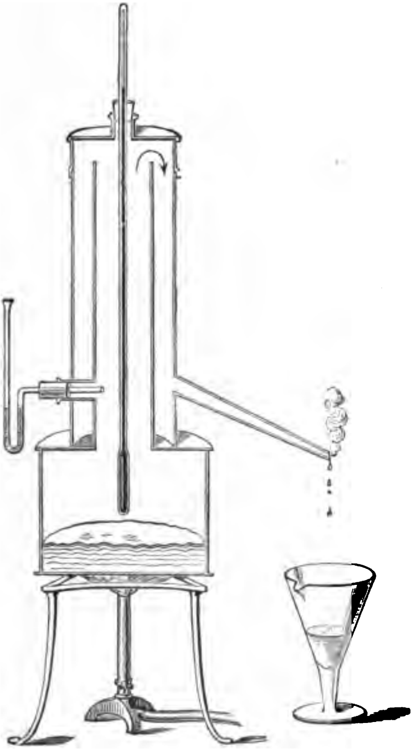

FIG. 6.—Arrangement for Determining the Boiling Point of a Thermometer.

EXPT. 5.—You are provided with a mercury thermometer, and an apparatus similar to that shown in Fig. 6. You are required to test the accuracy of the boiling point graduation (100° C.).

Care must be taken, in the first place, that steam has been given off copiously during some minutes before a reading is taken; and secondly, that no obstruction is opposed to the escape of the steam.

The upper part of the vessel in which the thermometer is placed is seen in Fig. 6 to consist of two concentric tubes, so arranged that the steam ascends the inner one, and escapes after having descended through the space between the two. By this means it is ensured that the metal tube nearest to the thermometer shall be at the temperature of the steam. Thus the temperature of the thermometer will not be lowered by radiation. (*See* Ch. XXI.).

It is best to arrange that the thermometer bulb is much higher above the water surface than is shown in Fig. 6. It is possible for the water to be at a temperature much above 100° C., and if any of this should be splashed on to the bulb errors might ensue.

Read the Barometer the moment after you make your final observation, at the same time noting the temperature of the air near the Barometer. The necessary corrections to be applied will be explained in Chapter II.

EXPT. 6.—After having determined the reading of the thermometer, when the bulb and the whole of the mercury column are surrounded by steam, withdraw the thermometer by about 10 degree divisions at a time, and note the temperature indicated in each case. The part of the mercury column not surrounded by steam is called the *exposed column*. Enter your results in a table similar to the following :—

Length of Exposed Column.	Reading.	Error due to Exposed Column.

Different Thermometric Scales.—We have heretofore considered only the Centigrade thermometric scale, in which the freezing point of water is defined as 0°, and the boiling point as 100°, the intermediate temperatures consequently comprising 100 degree divisions. This system is now used in scientific work all over the world.

The Fahrenheit scale of temperature is characterised by the boiling point of water being defined as 212°, while the freezing point of water is 32°; hence there are 180 degrees between the freezing and boiling points. The origin of the scale appears to have been as follows :—

When the temperature of a given mass of mercury is raised from the freezing point to the boiling point of water, the volume of the mercury is increased by about 180/10,000ths of its value at the freezing point (see p. 81). Hence if there are 180 degrees of temperature between the freezing and boiling points of water, a given mass of mercury will expand by 1/10,000th part of its volume at the freezing point, for every degree through which its temperature is raised. Further, the mercury will lose 1/10,000th of its volume at the freezing point, for every degree through which it is cooled below that temperature. Fahrenheit found that at the lowest temperature he could obtain by mixing ice and salt together a given mass of mercury had lost 32/10,000ths of the volume it possessed at the freezing point of water, and he defined this temperature as zero ; hence the freezing point of water became 32°, and the boiling point of water became 32+180=212° on the Fahrenheit scale.

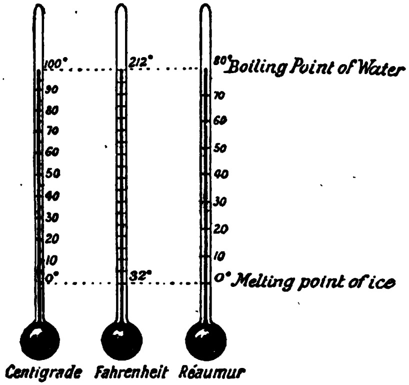

FIG. 7.—Comparison of Different Thermometric Scales.

The Fahrenheit scale of temperature is in general use in England, both for domestic purposes and by engineers. It has nothing to recommend it but its wide-spread acceptance.

In the Réaumur system the freezing point of water is defined as 0°, the boiling point of water being defined as 80°. This scale is used for domestic purposes in some parts of the Continent, but has no special advantage.

In converting a temperature from one system to another, the following system of reasoning must be employed :—

The interval of temperature between the boiling and freezing points of water is equal—

On the Centigrade scale, to 100 − 0 = 100°.
„ „ Fahrenheit „ „ 212 − 32 = 180°.
„ „ Réaumur „ „ 80 − 0 = 80°.

Consequently an *interval of temperature* $t°$ C. is equal to $\frac{t° \times 180}{100} = \frac{t° \times 9}{5}$ in the Fahrenheit scale. If t° denotes a temperature indicated by a Centigrade thermometer, then the corresponding temperature on the Fahrenheit scale will be equal to

$$\frac{t° \times 9}{5} + 32°.$$

Consequently we have the following relations :—

$$\text{Fahrenheit temp.} = \frac{\text{Cent. temp.} \times 9}{5} + 32 = \frac{\text{Réaumur temp.} \times 9}{4} + 32.$$

$$\text{Centigrade temp.} = \frac{(\text{Fah. temp.} - 32) \times 5}{9} = \frac{\text{Réaumur temp.} \times 5.}{4}$$

Example.—The B.P. of sulphur under normal atmospheric pressure is 444·5° C. What temperature will be indicated by a Fahrenheit thermometer when immersed in the vapour of sulphur boiling under normal pressure ?

$$\text{The required temperature} = \frac{444{\cdot}5 \times 9}{5} + 32 = 832{\cdot}1° \text{ F.}$$

Example.—Assuming the temperature of the blood of a healthy man to be 98° F., what temperature would be indicated by a Centigrade thermometer after the bulb has been placed for a short time in the mouth of such a person ?

$$\text{The required temperature} = \frac{(98 - 32)\,5}{9} = 36{\cdot}7° \text{ C.}$$

Sensitive Mercury Thermometers.—In order that it may be possible to read a temperature with great accuracy, it is obvious that the extremity of the mercury column should move through a considerable distance along the stem for a small alteration of temperature. Consequently, if such a thermometer is to be used for measuring temperatures from 0° C. to 100° C., either a very long stem must be provided, or some modification of the usual form must be employed.

The most usual procedure is to furnish the upper extremity of the thermometer tube (which is bent over as shown in Fig. 8), with an enlargement into which part of the mercury can be driven by heating. A sufficient amount of mercury must be left in the bulb and stem to give readings between the required temperatures. Fig. 8 represents a thermometer of this description. The following points in its construction may be noted.

In order to avoid the errors due to the irregular motion of the mercury in a very fine tube, a tube of comparatively large bore is employed. It has already been pointed out that the sensitiveness of a thermometer depends on the ratio, Volume of bulb : Sectional area of bore of tube, and as the bore is made comparatively large, a very large bulb is required. The stem is provided with an enlargement into which part of the mercury can be driven, for reasons explained above. The thermometer tube is made with comparatively thin walls, and to protect it from injury it is contained within a wider tube, which is fused at its lower extremity on to the bulb. The graduations are marked on a separate enamelled scale placed behind the thermometer tube, and inclosed in the outer guard tube. In order that this thermometer should be capable of furnishing readings for very quick changes of temperature, the walls of the bulb must be made very thin. This of course will expose it to considerable errors due to variations of pressure. (*See* Chapter II.).

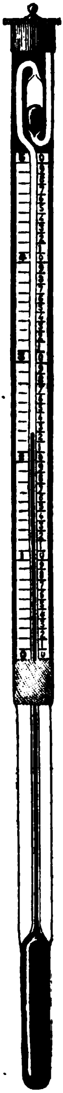

FIG. 8.—Sensitive Mercury Thermometer.

The fixed points of such a thermometer obviously cannot be obtained in the manner previously described. Its scale must be calibrated by comparison with a standard thermometer. Such a thermometer as that considered is, however, more often used to measure *small changes of temperature* than to determine actual temperatures.

Alcohol Thermometers.—The expansion of a given volume of alcohol or ether, when heated through 1° C., is, roughly speaking, about ten times as great as the expansion of an equal volume of mercury under similar conditions. Hence a given bulb and tube will form a much more sensitive thermometer when filled with alcohol than when filled with mercury. An alcohol thermometer consequently possesses the following advantages over a similar mercury thermometer.

Advantages of an Alcohol Thermometer:—

1. For a given size of bulb and tube, an alcohol thermometer will be more sensitive than a mercury thermometer; or, for a given sensitiveness, the bulb of an alcohol thermometer may be made ten times smaller than that of a mercury thermometer with a stem of the same bore.

2. Alcohol being much less dense than mercury, variations in the internal pressure are less to be feared. (*See* Chapter II.)

3. When a thermometer is immersed in a liquid the temperature of which is required, the thermometer is heated and the liquid is cooled. When an alcohol thermometer is used, the extent of the cooling is smaller than when an equally sensitive mercury thermometer is employed. This may be proved as follows:—

We have seen that for a given sensitiveness and bore of the tube, the bulb of an alcohol thermometer need only enclose about $\frac{1}{10}$th of the volume necessary for a mercury thermometer. Let v = the volume of the bulb of the mercury thermometer; the $\frac{v}{10}$ = the volume of the bulb of the alcohol thermometer. The density of mercury is about 13·6; whilst that of alcohol is about ·8. Consequently, mass of alcohol used $= \frac{v}{10} \times {\cdot}8$. Mass of mercury used $= v \times 13{\cdot}6$.

The specific heat of mercury may be taken roughly as ·03; whilst that of alcohol = ·6 (*See* Chapter VI.). Hence the quantity of heat required to raise the temperature of the alcohol through 1° C. $= \frac{v}{10} \times {\cdot}8 \times {\cdot}6 = v \times {\cdot}048$. The quantity of heat required to raise the temperature of the mercury through 1° C. $= v \times 13{\cdot}6 \times {\cdot}03 = v \times {\cdot}408$. Hence we see that a much smaller quantity of heat is required to raise the temperature of the alcohol in a thermometer through 1° C. than would be necessary for the mercury in a thermometer of equal sensitiveness. Hence a warm liquid will be cooled to a smaller extent by the introduction of an alcohol thermometer than if a mercury thermometer of equal sensitiveness had been employed.

4. Since the alcohol wets the sides of the tube, it has no tendency to stick as mercury has, so that the expansions are quite regular. Irregularities in the motion of the thread of a mercury thermometer are very objectionable when the *rate of change* of temperature is required. In such cases an alcohol thermometer might advantageously be used.

5. Since the ratio of the expansion of alcohol to that of glass is much greater than the ratio of the expansion of mercury to that of glass, errors introduced by variations in the volume of the bulb will be of less importance in the case of an alcohol thermometer than in the case of a mercury thermometer.

6. Mercury becomes solid at $-39°$ C.; whilst alcohol remains liquid to about $-130°$ C. Hence an alcohol thermometer may be used for low temperature work for which a mercury thermometer would be useless.

Disadvantages of Alcohol Thermometers:—

1. Alcohol boils at about 78° C., so that an alcohol thermometer must never be heated to a temperature above 60° C. Consequently we cannot obtain the upper fixed point by immersing the thermometer in steam. The scale must be calibrated by comparison with a standard thermometer.

2. When the bulb of an alcohol thermometer is placed in warm water, the upper part of the thermometer stem being kept cool, alcohol distils into the free space and condenses on the walls there. This can be prevented by keeping the upper part of the stem as warm as, or warmer than, the bulb.

3. It is difficult entirely to free the alcohol from air before sealing off, with the consequence that after that operation has been performed, small air bubbles often make their appearance in

the alcohol contained in the stem or the bulb. These bub can generally be shaken up into the free part of the tube ; the operation is tedious. A solution of 10 or 15 per cen anhydrous calcium chloride in alcohol is said not to possess disadvantage.

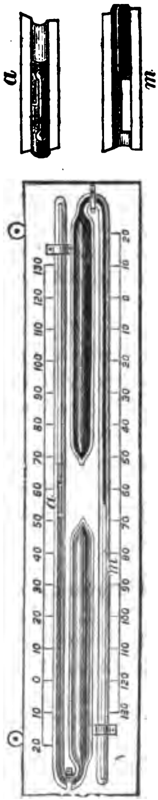

FIG. 9.—Rutherford's Maximum and Minimum Thermometer. (P.)

4. Since, in an alcohol thermometer, sectional area of the bore of the tube n be larger in comparison with the volum the bulb than in a mercury thermomete: equal sensitiveness, a greater proportior the whole of the thermometric substa will generally be in the tube in an alco than in a mercury thermometer. Con quently the error due to the exposed colu being at a lower temperature than the bu will be greater in an alcohol than in a m cury thermometer.

Maximum and Minimum Therm meters.—It is sometimes necessary determine the highest or lowest tempe ture which has been indicated by a therm meter during a certain time. Special for of thermometers are used for this purpos

Fig. 9 represents *Rutherford's maxim and minimum thermometer.* An alcol thermometer is used for registering t minimum temperature. A small piece thin glass rod has knobs melted on it each end, and this index, *a*, is immersed the alcohol in the stem (which is mai tained horizontal) ; the alcohol surface dra the index backward when the temperatu falls, but leaves it stationary when a ri occurs. This is due to the surface tensic of the alcohol ; for a similar reason a need may be floated on the surface of wate The index is re-adjusted by tilting the thermometer.

A mercury thermometer is used to register the maximu temperature. A small piece of iron, *m*, is inserted in the ste above the mercury, and is pushed before the latter as the tem perature rises. It can be brought back to the mercury surface by the aid of a magnet.

In *Six's self-registering thermometer* (Fig. 10) the bulb A is filled with alcohol or a similar liquid, and this extends to B, one surface of a mercury thread BC. Above C there is more alcohol, which partly fills the bulb D, leaving, however, a space for expansion. Two steel indexes, provided with springs just strong enough to prevent them from slipping, are respectively situated above the free ends of the mercury thread. When the temperature rises, the index is pushed before the mercury surface at C, and is left in position when a fall of temperature causes the mercury to withdraw. Thus the maximum temperature is registered. Similarly, the minimum index is moved when the mercury surface at B comes in contact with it, and is left in position when a rise of temperature takes place.

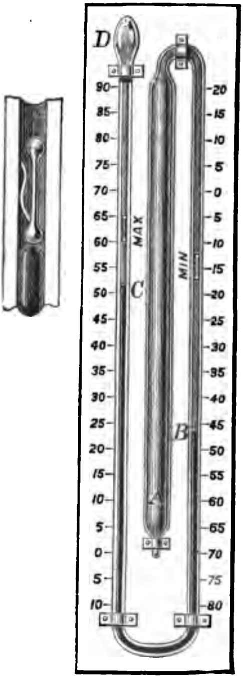

FIG. 10.—Six's Self-registering Thermometer. (P.)

In *Negretti and Zambra's maximum thermometer* there is a constriction in the tube just above the bulb, so that as the temperature rises the mercury is extruded, whilst a subsequent fall of temperature causes the mercury column to break at the constriction, leaving the mercury in the tube in the position which it occupied when the temperature was a maximum. The maximum temperature is thus read directly from the position of the upper end of the mercury column. The mercury can be shaken back into the bulb when a new reading is to be taken.

Fig. 11 represents a Clinical thermometer constructed in this manner, the temperatures which it can indicate being confined within the limits 95° F. and 113° F.

In *Phillips' maximum thermometer* (Fig. 12) a short thread of mercury is separated from the rest of the mercury in the stem by a small air bubble. The detached thread acts like the index shown in Fig. 10. The illustration shows such a thermometer mounted in a strong glass tube for deep sea soundings. The space between the thermometer and the guard tube is partly filled with alcohol, so as to ensure a good thermal communication between the thermometer bulb and the surrounding medium.

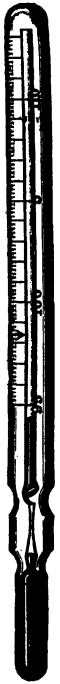

FIG. 11.—Clinical Thermometer. (P.)

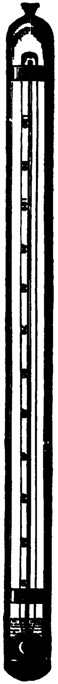

FIG. 12.—Phillips' Maximum Thermometer. (P.)

High Temperature Thermometers.—Under normal pressure mercury boils at 357° C., so that an ordinary mercury thermometer cannot be used above that temperature. This inconvenience may to some extent be overcome by filling the space above the mercury with compressed nitrogen, so that the mercury is prevented from boiling by the high pressure to which it is subjected (*see* Chapter VIII). The bulb must necessarily be made very strong, and even then, if a thermometer of this class is maintained for some time at a high temperature (400° C. or so), the zero will often be found to have changed considerably when cooling takes place. *Metallic Potassium* and *Sodium* when mixed form a peculiar alloy, which presents very much the appearance of mercury, and is liquid at ordinary temperatures. This has been successfully employed in the construction of high temperature thermometers. These may be used at temperatures considerably above those admissible for ordinary mercury thermometers. The bulb and stem are made of hard Jena glass.

Gas Thermometers.—The high expansion of gases renders them especially suitable for thermometric substances, as in their case expansions of the containing vessel produce comparatively small effects on the accuracy of the observed temperature. As, however, the theory of their action depends on certain laws which will be developed later, their consideration is deferred for the present. (*See* Chapter V.)

SUMMARY

The term "**temperature**" is used to denote the hotness of a body. Our ideas of temperature are primarily derived from our sensations, but in order to determine temperatures accurately, some physical property which varies continuously with the temperature must be measured.

A thermoscope indicates the attainment of a particular temperature.

A thermometer is an instrument designed to measure temperatures. Mercury expands when heated; and this property is utilised in the construction of mercury thermometers. Various forms are given to these instruments, according to the purpose for which they are to be employed.

In all cases two **fixed points**, corresponding to two arbitrary temperatures, are selected, and the difference between these temperatures is divided into an arbitrary number of degrees.

On the **Centigrade scale** the temperature of melting ice is taken as 0°. The temperature of the steam above water boiling at standard atmospheric pressure is defined as 100°.

On the **Fahrenheit scale**, temperature of melting ice = 32°, temperature of boiling water = 212°.

On the **Réaumur scale**, temperature of melting ice = 0°, temperature of boiling water = 80°.

A sensitive mercury thermometer must either be furnished with a very long stem, or a receptacle must be provided, into which part of the mercury can be driven when occasion requires. The latter procedure is most frequently followed.

A maximum thermometer is used to record the highest temperature attained during a given time.

A minimum thermometer is used to record the lowest temperature attained during a given time.

In **high temperature mercury thermometers**, ebullition is prevented by subjecting the mercury to a high pressure. In other cases an alloy of sodium and potassium is substituted for mercury.

QUESTIONS ON CHAPTER I.

(1) Describe some of the principal forms of maximum and minimum thermometers.

(2) Find the Centigrade temperatures corresponding to 68° F., 176° F., −20° F., and the Fahrenheit temperatures corresponding to 4° C., 52° C., and −273° C.

(3) What peculiarities of construction may be noticed in a sensitive mercury thermometer?

(4) Explain how you would proceed to determine the error due to the exposed column of a thermometer.

(5) Describe the process of determining the fixed points (melting ice and boiling water) of a mercury thermometer, and point out any precaution that ought to be observed.

A thermometer with an arbitrary scale of equal parts reads 14·6 in melting ice and 237·9 in water boiling under standard pressure. Find the Centigrade temperatures indicated by the readings 97·1 and 214·0 on this thermometer.

(6) State what means you would employ to measure (1) a very high temperature, (2) a very small difference of temperature. (See also Ch. XIX.)

CHAPTER II

ERRORS OF A MERCURIAL THERMOMETER, WITH THEIR CORRECTIONS

(THE reading of this chapter may, if necessary, be postponed till after Chapters III. and IV. have been read.)

Correction to be applied in order to determine the true Boiling-point.—The boiling-point of a liquid varies with the pressure to which it is subjected. The standard pressure adopted is equal to the force exerted by gravity on a vertical column of mercury 76 cm. long, and possessing a sectional area of 1 sq. cm., the mercury being at the temperature 0° C., and being placed at the sea level in latitude 45°.

Fig. 13 represents *Fortin's Barometer*, the instrument most commonly used for determining the pressure of the atmosphere. A long glass tube is entirely filled with mercury, and then inverted, and placed with its lower extremity in a mercury reservoir R. The height of the surface of the mercury in the tube, above the level of the mercury in the reservoir, gives the barometric height. In order to maintain the surface of the mercury in the reservoir at a constant level, the lower part of the reservoir is made of leather (Fig. 14), and this can be raised or lowered by the aid of a screw, A (Fig. 13), till the mercury surface coincides with the point of an ivory pin P. The graduations on the scale S represent heights above the point of the pin P.

The barometer having been read, the following corrections

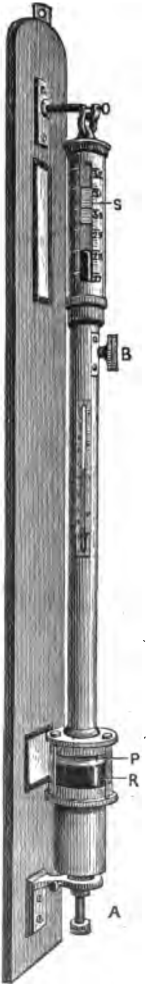

FIG. 13.—Fortin's Barometer.

will be necessary before the true atmospheric pressure can be determined.

1. Correction for the temperature of the mercury.

2. Correction for the expansion of the scale attached to the barometer.

3. Correction for the latitude of the place where the barometer is placed.

4. Correction for the height above the sea level.

These corrections will now be considered.

1. *Temperature Correction for the Mercury.*—The density of mercury varies with the temperature. Since the weight of the barometric column, supposed to have a sectional area of 1 sq. cm., just balances the weight of a column of the atmosphere possessing a like sectional area, it follows that a decrease in the density of mercury will correspond to a longer barometric column, and *vice versa.*

Let us suppose that the scale and the tube containing the mercury are maintained at 0° C., whilst the temperature of the mercury is raised from 0° to t° C. The same mass of mercury will in both cases balance the atmospheric pressure, but owing to the expansion of the mercury, the latter will occupy a greater volume at the higher temperature.

Let h_0 = the height of the mercury column, when the temperature of the mercury = 0° C.

Let h_t = the height of the mercury column, when the temperature of the mercury = t° C.

Then since the sectional area of the column is in each case equal to 1 sq. cm., we have, if h_0 and h_t are measured in cms.,

Volume of mercury at 0° C. = $h_0 \times 1 = h_0$ c.cs.
" " t° C. = $h_t \times 1 = h_t$ c.cs.

Let a = the coefficient of cubical expansion of mercury; *i.e.*, the increase in volume of

1 c.c. of mercury, when its temperature is raised through 1° C.

Then, as proved on p. 59, it follows that

h_0 c.cs. at 0° correspond to $h_0(1 + at)$ c.cs. at t° C.

$$\therefore h_t = h_0(1 + at).$$

$$\therefore h_0 = \frac{h_t}{1 + at} = h_t(1 - at + a^2t^2 \; . \; .$$

expanding by the binomial theorem. When t is small, the product a^2t^2, and higher powers of (at), may be neglected.

$$\therefore h_0 = h_t(1 - at) \quad . \; . \; . \; . \; . \quad (1)$$

We thus see that our first correction is obtained by multiplying the observed barometric height, h_t, by $(1 - at)$. According to Regnault

$$a = \cdot0001802 \text{ (p. 81)}.$$

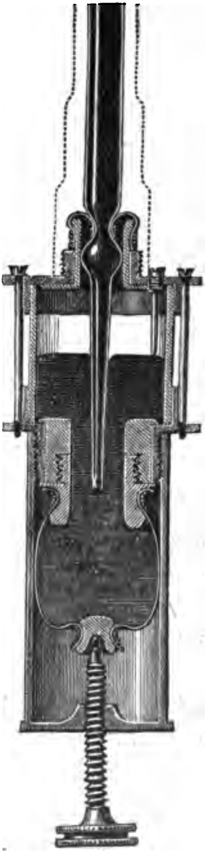

FIG. 14.—Mercury Reservoir of Fortin's Barometer.

2. *Correction for Expansion of the Scale, which is supposed to be correct at* 0° C.—The true distance between two marks on a scale will increase as the temperature of the scale is raised. The amount of the increase in any particular case will depend

(*a*) On the initial distance between the marks,

(*b*) On the substance on which the scale is engraved. In the Fortin barometer (Fig. 13) the scale is engraved on brass. In this case 1 cm. length engraved on brass at 0° C., will increase to $(1 + \beta)$ cm. at 1°, and to $(1 + \beta t)$ cm. at t° C.; β being approximately equal to ·000020.

∴ a distance h_0 cms. measured on the brass scale at t° C. is equal to a true distance of

$$h_0(1 + \beta t) \text{ cms.} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Combining the corrections (1) and (2), we obtain—

Height of barometer, corrected for temperature,
$= H = h_0(1 + \beta t) = h_t(1 - at)(1 + \beta t) = h_t(1 - (a - \beta)t - a\beta t^2)$.

Neglecting the term $a\beta t^2$, which will be very small, since both a and β are small, we finally have

$$H = h_t(1 - (a - \beta)t) = h_t(1 - (\cdot000182 - \cdot000020)t)$$
$$= h_t(1 - \cdot000162t) \ldots .$$

Another correction which should be applied is that due to the surface tension of the mercury. Owing to the curvature of the surface of the mercury, the latter will stand at a lower level in narrow barometer tubes than in wide ones. This correction is best made by comparison with a barometer possessing a very wide tube.

3. *Correction for the Latitude.*—The attraction of gravity at the surface of the earth decreases with the distance of the surface from the centre of the earth. Owing to the spheroidal shape of the earth, the mean equatorial diameter is greater than the polar diameter, and consequently the attraction of gravity is less at the equator than at the poles. The attraction of gravity at points on the parallels of latitude 45° N. or S. of the equator is chosen as a standard, and the attraction at a point in latitude λ will be equal to

Attraction at a point on the 45th parallel $\div (1 + B \cos 2\lambda)$, where $B = 0\cdot00256$.

Let h be the correct height of a column of mercury at 0° C., which produces, at a place in latitude λ, a pressure equal to that of the standard column, 760mm. long, at the sea level in lat. 45°.

Then

$$\frac{h}{1 + B\cos 2\lambda} = 760\text{mm.}$$

$$\therefore\ h = 760\,(1 + B \cos 2\lambda)$$
$$= 760 + 1\cdot9546 \cos 2\lambda.$$

4. *Correction for Height above the Sea Level.*—For similar reasons to those explained in considering correction (3), the length of a column of mercury which produces the standard

pressure, increases with the height above the sea level. The total correction for (3) and (4) may be expressed as follows :—

Standard length of barometric column, the mercury being at 0° C., at a point in latitude λ, and at a height h (in feet) above the sea level

$$= H_0 = 760 + 1{\cdot}9456 \cos 2\lambda + 0{\cdot}00004547h$$

measured in millimetres.

Having in the manner explained determined the true barometric pressure, we can proceed to obtain the temperature of the vapour over the boiling water. This can be done by reference to the following table :—

BOILING POINT OF WATER AT DIFFERENT PRESSURES.

(The pressures are given in mm. of mercury at a temperature of 0° C., situated at the sea level in lat. 45°.)

mm.	°	mm.	°	mm.	°	mm.	°
733	98·9939	745	99·4449	757	99·8897	769	100·3286
734	99·0318	746	·4822	758	·9265	770	·3649
735	·0695	747	·5194	759	·9633	771	·4012
736	·1073	748	·5567	760	100·0000	772	·4374
737	·1449	749	·5938	761	·0367	773	·4736
738	·1826	750	·6310	762	·0733	774	·5098
739	·2202	751	·6681	763	·1099	775	·5459
740	·2577	752	·7051	764	·1465	776	·5820
741	·2953	753	·7421	765	·1830	777	·6180
742	·3327	754	·7791	766	·2194	778	·6540
743	·3702	755	·8160	767	·2559	779	·6900
744	·4075	756	·8529	768	·2923	780	·7259

If the thermometer reading was 100° C. when the bulb and stem were surrounded by steam, then the difference between 100° C. and the temperature obtained from the above table, corresponding to the true pressure to which the water was subjected, will give the error in the boiling-point of the thermometer. An example will best explain the course to be followed.

EXAMPLE.—A thermometer, graduated in half degrees, after being surrounded for half an hour by steam in an apparatus such as shown in Fig. 6, indicated a temperature of 98·55 °C. Barometer reading = 758·2 mm. Temperature indicated by thermometer attached to barometer = 14·5° C. Latitude of observing station = 53° N. Height of observing station above sea level = 120 feet.

1. Correction for temperature of barometer

$$h_0 = h_t(1 - \cdot 000162t)$$
$$h_0 = 758\cdot 2\,(1 - \cdot 000162 \times 14\cdot 5)$$
$$= 758\cdot 2\,(1 - \cdot 00235) = 758\cdot 2 \times \cdot 99765 = 756\cdot 4 \text{ mm.}$$

(It is assumed that the barometer could only be read to ·1 millimetre).

Standard barometric height at station—

$$= 760 + 1\cdot 9456 \cos(2 \times 53^\circ) + 0\cdot 0000455 \times 120.$$
$$= 760 - 1\cdot 9456 \sin 16^\circ + 0\cdot 0000455 \times 120.$$
$$= 760 - \cdot 5360 + \cdot 00546$$
$$= 759\cdot 5 \text{ mm. (approximately).}$$

It will be observed that the correction for height is too small to be taken into account. Indeed, with a barometer reading to a hundredth of a millimetre, no correction need be applied for points at an elevation of less than 220 feet above the sea level. On the other hand, it will be observed that the correction for latitude should generally be applied in England.

Hence, a barometric reading of 759·5 mm. at the station in question corresponds to standard pressure, *i.e.*, to 760 mm. in latitude 45°.

∴ A barometric reading of 756·4 mm. corresponds to

$$\frac{756\cdot 4 \times 760}{759\cdot 5} = 756\cdot 8 \text{ mm. in the table on p. 27.}$$

From this table, we find that

At a pressure of 756 mm. water boils at 99·85° C.
" " 757 " " 99·89° C.

∴ at a pressure of 756·8 mm. water boils at 99·88° C.

Consequently, when the thermometer in question reads 98·55° C., the true temperature is 99·88° C.

∴ Correction to be applied to reading for boiling point = + 1·3° C.

This example, when carefully followed, exhibits not only the method of applying the correction, but also the error which would have been introduced in our final results had the corrections of the barometer reading not been applied. Thus, using simply the observed barometric height, we obtain from the above table,

At 758·2 mm. water boils at 99·94° C. about.

∴ correction to be applied = 99·94 − 98·55 = 1·39°.

Since, by eye observation, we can only estimate the temperature to ·1 of ½ a degree, *i.e.*, to ·05°, it at once becomes evident that the difference between the true correction and that obtained without reducing the pressure to standard conditions, is almost within the limits of experimental error. In this case it was hardly necessary to go through the above calculations. On the other hand, when using thermometers graduated in $\frac{1}{50}$ths of degrees, the above procedure should be followed.

EXPT. 7.—From the temperature indicated by your thermometer, when placed in steam from water boiling under an observed pressure, as determined in the experiment on p. 11, Chap. i., obtain the true boiling point error of your thermometer.

Correction for Inequalities in the Bore of the Thermometer Tube.—If the bore of the thermometer tube is uniform, then a given mass of mercury would form a thread of the same length, in whatever part of the tube it was situated. It has already been remarked that this test is used in the selection of suitable thermometer tubes. It is almost impossible, however, to obtain tubes of which the section is uniform throughout, especially when those with an elliptical or flattened bore are used. Consequently the thermometer having been constructed as previously described, and its fixed points determined and the stem graduated, the next point of importance is to obtain the correction to be applied to any particular reading due to the small irregularities of the bore.

When a thermometer possesses a constriction just above the bulb, a thread of mercury will generally detach itself at that point if the thermometer is inverted. A slight jerk while the thermometer is in the latter position will sometimes be found necessary. In order to obtain a detached thread of mercury of any desired length, a piece of cotton wool soaked in ether may be wound round the thermometer bulb, which can then be cooled by blowing air on it. When the length of the thread beyond the constriction is suitable, the thermometer may be inverted, and that length detached.

A thread of mercury of any desired length can also be detached by applying a small gas flame to the thermometer tube at a position sufficiently far from the extremity of the column. A suitable gas burner may be made from a piece of glass tubing drawn out to a rather fine point (Fig. 15). The mercury boils at the point heated, and the part of the thread beyond this point is detached, and may be shaken to any position in the thermometer tube. It should, when possible, be arranged that the heated point lies outside the part of the tube for which corrections are to be determined, since the glass expands rather considerably at the point which is heated, and only reattains its normal section after some time. Further, some difficulty is generally experienced in subsequently shaking the detached mercury thread past the point which has been heated, and moreover an error may be introduced if mercury has been condensed in small globules in the neighbourhood. On the other hand, the thermometer must not be heated too close to the junction between stem and bulb, or a fracture will inevitably result. When due care is taken, a thermometer is rarely broken whilst a thread is being detached in this manner. It is preferable, however, to use the method first described whenever possible.

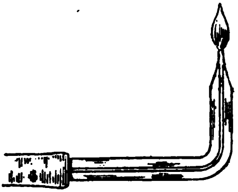

FIG. 15.—Gas Jet for Detaching Mercury Thread.

The next point to be determined is the length of the detached thread, *measured in scale divisions*, at various points of the thermometer stem. It is commonly recommended in text books on Heat that these measurements should be effected by the aid of a travelling microscope. In cases where subsequent readings of the thermometer are to be made with the aid of a telescope this procedure might be advantageous; it is probable, however, that even in this case the corrections obtained would not give the true temperature without the employment of a great number of other corrections, necessitated by circumstances which will be subsequently considered. In the case of a thermometer which is only to be employed for eye observations, the use of a travelling microscope to determine the length of the thread is quite unnecessary, as it would only result in the corrections exceeding in accuracy the readings to which they are to be applied.

Let us suppose that Fig. 16 represents a part of the thermometer stem together with the detached thread *ab*. It is convenient to arrange the length *ab* to be equal, as nearly as possible, to 10 thermometer scale divisions; on the other hand, the accuracy of the curve of corrections finally obtained will be the greater if the mercury thread is shorter.

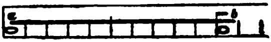

FIG. 16.—Part of Thermometer Stem showing Detached Thread.

If, now, the thermometer graduations represented equal increments of volume, the mercury thread would have the same length in different parts of the tube. This will seldom be the case, and we must proceed to determine the corrections δ_0, δ_{10}, δ_{20}, &c., which must be applied to the reading taken for the ends of the mercury thread, when these coincide approximately with the graduations marked 0° and 10°, 10° and 20°, &c.

In Fig. 16 the length from *a* to the 1° graduation is approximately equal to ·6°, whilst the distance from the 10° divisions to *b* is about ·8°. Hence

$$\text{Length of thread} = l_1 = 9^\circ + \cdot6^\circ + \cdot8^\circ$$
$$= 10\cdot4^\circ.$$

l_2 will be determined in a similar manner, *a* being now in the neighbourhood of 10°, and *b* in the neighbourhood of 20°. Proceeding in a similar manner to obtain l_3, l_4, &c., the first two columns in the Table on p. 32 may be constructed.

The various values, l_1, l_2, &c., might have been obtained by noting the position of *a* and *b* on the thermometer scale, and subtracting one from another. Thus, for l_1,

a is at 0·4°, *b* is at 10·8°.

$$\therefore\ l_1 = 10\cdot8 - 0\cdot4 = 10\cdot4^\circ.$$

On the other hand, if the graduations had been correct, we should have obtained a constant value L for the length of the thread whatever its position might have been in the tube. Taking δ_0 as the correction to be added to readings in the neighbourhood of 0°; δ_{10}, that to be added to readings near 10° &c., &c., we have

$$L = (10\cdot8 + \delta_{10}) - (0\cdot4 + \delta_0)$$
$$= l_1 + \delta_{10} - \delta_0.$$

Similarly,

$$L = l_2 + \delta_{20} - \delta_{10}$$
$$L = l_3 + \delta_{30} - \delta_{20}$$
$$\ldots = \ldots\ldots\ldots$$
$$\ldots = \ldots\ldots\ldots$$
$$L = l_{10} + \delta_{100} - \delta_{90}.$$

Adding all of these equations together, we get

$$10L = l_1 + l_2 + l_3 + \ldots\ldots + l_{10} + \delta_{100} - \delta_0.$$

δ_{100} will, of course, be the boiling point correction, whilst δ_0 will be the freezing point correction. We may for the present assume both these to be zero; if they are not, a graphical correction can be applied later on. Hence $L = \frac{l_1 + l_2 + l_3 + \ldots\ldots + l_{10}}{10}$ = the mean value of the thread length, measured in scale divisions.

From the first of the above equations (remembering that $\delta_0 = 0$)

$$\delta_{10} = L - l_1 = \phi_1 \text{ (say).}$$

Similarly, $\delta_{20} = L - l_2 + \delta_{10} = \phi_2 + \phi_1$, if $\phi_2 = L - l_2$

$\delta_{30} = L - l_3 + \delta_{20} = \phi_3 + \phi_2 + \phi_1$, if $\phi_3 = L - l_3$

$\ldots = \;\ldots\ldots \quad \ldots\ldots \quad \ldots\ldots$

$\delta_{90} = L - l_9 + \delta_{80} = \phi_9 + \phi_8 + \;.\;.\; + \phi_1$, if $\phi_9 = L - l_9$

$\delta_{100} = 0$ (boiling point assumed correct).

Hence, to find the corrections to be applied to readings in the neighbourhood of 10°, 20° . . . 90°, 100°, we proceed as follows.

1. Find the mean thread length L, as above.

2. Successively subtract l_1, l_2, l_3, . . . &c. (the observed thread lengths), from L.

3. The result obtained by subtracting l_1 is δ_{10}; the algebraical sum of the quantities obtained by successively subtracting l_1 and l_2, is δ_{20}; and so on. We can now construct a table of corrections for the various readings.

Position of Thread between	Thread Length.	Difference from Mean.	Corrections.
0° and 10°	$l_1 = 10{\cdot}4$	$L - l_1 = -{\cdot}17$	$\delta_{10} = \phi_1 = -{\cdot}17 = -{\cdot}2^\circ$ nea
10° ,, 20°	$l_2 = 10{\cdot}6$	$L - l_2 = -{\cdot}37$	$\delta_{20} = \phi_1 + \phi_2 = -{\cdot}54 = -{\cdot}5^\circ$,,
20° ,, 30°	$l_3 = 10{\cdot}7$	$L - l_3 = -{\cdot}47$	$\delta_{30} = \phi_1 + \phi_2 + \phi_3 = -1{\cdot}01 = -1{\cdot}0^\circ$,,
30° ,, 40°	$l_4 = 10{\cdot}5$	$L - l_4 = -{\cdot}27$	$\delta_{40} = -1{\cdot}28 = -1{\cdot}3^\circ$,,
40° ,, 50°	$l_5 = 10{\cdot}4$	$L - l_5 = -{\cdot}17$	$\delta_{50} = -1{\cdot}45 = -1{\cdot}4^\circ$,,
50° ,, 60°	$l_6 = 10{\cdot}4$	$L - l_6 = -{\cdot}17$	$\delta_{60} = -1{\cdot}62 = -1{\cdot}6^\circ$,,
60° ,, 70°	$l_7 = 10{\cdot}2$	$L - l_7 = +{\cdot}03$	$\delta_{70} = -1{\cdot}59 = -1{\cdot}6^\circ$,,
70° ,, 80°	$l_8 = 10{\cdot}0$	$L - l_8 = +{\cdot}23$	$\delta_{80} = -1{\cdot}36 = -1{\cdot}4^\circ$,,
80° ,, 90°	$l_9 = 9{\cdot}7$	$L - l_9 = +{\cdot}53$	$\delta_{90} = -{\cdot}83 = -{\cdot}8^\circ$,,
90° ,, 100°	$l_{10} = 9{\cdot}4$	$L - l_{10} = +{\cdot}83$	$\delta_{100} = -\;0 \;-\; 0^\circ$
	$L = 102{\cdot}3$	$\div 10 = 10{\cdot}23$	

It will be noticed that L is taken to the second place of decimals, whilst the observation values of l_1, l_2, &c., are only correct to the first place of decimals. But the errors made in estimating l_1, l_2, &c., will, on an average, as often be positive as negative ; hence we may fairly take L as approximately correct to two places of decimals. As a result of experience, it will be found that the corrections obtained from eye observations, as above, will seldom differ by as much as ·1 of a scale division from the more accurate values obtained by measuring the thread-length by means of a travelling microscope.

Marking the scale divisions of the thermometer horizontally on squared paper, and plotting the values δ_0, δ_{10}, δ_{20}, &c., vertically above 0°, 10°, 20°, &c., the points so found may be connected by means of a closed curve, and the correction for intermediate points determined therefrom (Fig. 17).

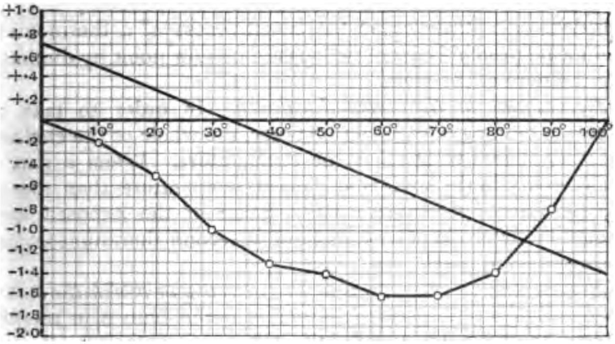

FIG. 17.—Correction Curve for Thermometer.

If, now, the freezing-point correction is plotted vertically below the 0° abscissa (if additive), or vertically above the 0° abscissa (if it must be subtracted from the observed reading), the boiling-point correction being plotted in a similar manner, and the two points finally joined by means of a straight line, then the correction to be applied to any observed reading may be read off as the vertical distance, along the appropriate ordinate, from the straight line to the curve. In Fig. 17, the B.P. correction is taken as + 1·4° C., the freezing-point correction being

−·7° C. The correction to be applied to a reading of 5° is equal to −0·6°, that is, the true temperature corresponding to a reading of 5° is equal to 4·4° C. Similarly, correction for reading of 12° is equal to −0·7°; for 90°, correction = +0·4°, &c., &c.

EXPT. 8.—Draw a curve of corrections for your mercury thermometer, obtaining the necessary data as previously described. The boiling point and zero corrections already obtained may be used.

Other Sources of Error in Mercury Thermometers.—*Errors due to capillarity.*—When a thermometer possesses a tube of very fine bore, the mercury does not move freely, but may remain stationary for some time in the stem, while the temperature is raised or lowered, and then suddenly alter its position. For this reason the sensitiveness of a thermometer cannot be profitably increased past a certain point by diminishing the bore of the stem.

Errors due to the exposed column.—In order to take an accurate reading with a thermometer, the whole of the enclosed mercury should be at the same temperature. When a part of the mercury in the stem is at a lower temperature than that in the bulb, the approximate temperature of the exposed stem should be determined by the aid of a second thermometer, and a correction applied.

Errors due to alterations in the pressure to which the bulb is subjected.—In order that the mercury in the bulb of a thermometer should quickly take up the temperature of a medium in which it is immersed, the walls of the bulb must be made thin. This introduces a new source of error, since any change in pressure will alter the volume of the bulb, and thus produce a motion of the mercury thread independently of any change in the temperature of the mercury. Alterations in pressure may be produced

(1) By variations in the barometric pressure.

(2) By variations of hydrostatic pressure, due to the bulb being placed at various depths below the surface of the same or different liquids.

(3) By variations in the internal pressure due to the extremity of the mercury column being at various heights above the centre of the bulb. With thermometers possessing very thin-walled

bulbs this is likely to produce considerable errors, since the head of mercury generally increases at a greater rate than the density of the mercury decreases.

Variations in the internal pressure are produced when the thermometer is sometimes used in a vertical, and sometimes in a horizontal position.

Corrections for these sources of error must be determined experimentally, and applied as the particular case requires.

Errors due to Softness of the Glass.—When a thermometer is heated, not only the mercury but the glass also expands.

EXPT. 9.—Plunge a tolerably sensitive thermometer into warm water; the mercury will be seen to sink for a short time, due to the expansion of the bulb, and then commence to rise as the enclosed mercury becomes heated and expands.

If a thermometer is heated considerably, the glass does not on cooling at once return to its initial state, but at first contracts quickly, until a volume slightly larger than the initial volume is reached, and then contracts very slowly, reaching its initial volume only after many months. This source of error may easily be demonstrated.

EXPT. 10.—Determine the freezing point before, and immediately after, the boiling point has been determined. The freezing point obtained after the thermometer has been immersed in steam is always slightly lower than that obtained when the thermometer has been kept at a low temperature for some time. The difference may amount to 1° C.

It has been found, that if a thermometer, before being sealed and graduated, is heated for a week or ten days to the temperature of boiling mercury, the zero point is much less altered by subsequent heatings. Hard glass thermometers also give less trouble in this respect than those made from soft glass.

There appears to be some amount of disagreement as to whether the freezing point should be determined before the boiling point is found, or *vice versa*. The freezing point which is most directly comparable with the boiling point is certainly that obtained directly after the latter has been found; only, it should be remembered that in making subsequent measurements, the thermometer should always be heated to the boiling point shortly before a reading is required to be taken.

Errors due to the heat capacity of the thermometer.—When a thermometer is placed in a warm liquid, the liquid will be cooled as the thermometer is heated. Hence, unless a very large quantity of liquid is used, the temperature indicated will be lower than that of the liquid before the thermometer was introduced.

Further, if a thermometer is placed in a bath of liquid of which the temperature is rising, the mercury in the thermometer will always be colder than the liquid. When the temperature of the bath is falling, the thermometer will always be warmer than the surrounding liquid.

From the above it will be seen that with a mercury thermometer, even if made by the best maker, the determinations of a temperature with accuracy is no easy task. *A temperature cannot be accurately determined within* $\frac{1}{100}$° C. *unless corrections for most of the above sources of error are applied.* Mr. Griffiths states that on comparing thermometers made by one of the best makers, the readings differed by as much as ·4° C. After applying corrections, obtained from tables which had been furnished for the different instruments by the Bureau of Weights and Measures at Paris, the final results never differed by more than 0·010° C., and only in one instance by more than 0·006° C.

Although the measurement of a temperature is a matter of so much difficulty, differences of temperature may be much more easily measured. Thus a thermometer, of which the boiling- and freezing-points are considerably wrong may often be used to obtain differences of temperature not greater than a few degrees without any great fear of committing grave errors.

SUMMARY

The most usual method of determining temperature is by means of a mercury thermometer. In the Centigrade system, the temperature of water boiling at a standard pressure is taken as 100°. The standard pressure alluded to is equivalent to the weight of a column of mercury 760 mm. in length, and possessing a sectional area of 1 sq. cm., placed at the sea level in latitude 45°. The temperature of melting ice is taken as 0° C. The part of the thermometer stem between the points respectively occupied by the end of the mercury thread, when the whole of the contained mercury is at the above temperatures, is divided into 100 equal parts. Each part corresponds to a degree Centigrade. In order to obtain the temperature of a liquid with accuracy (let us say to within $\frac{1}{100}$° C.), the following operations must be performed :—

(1) Determination of the boiling-point error.

(2) Determination of the freezing-point error.

(3) Calibration of the bore of the tube.

(4) Determination of the temporary changes of zero, making repeated observations of its permanent rise.

(5) Estimation of differences caused by movements from the horizontal to the vertical position.

(6) Observations of the effect of changes of external pressure.

(7) Determination of the differences resulting from the rate of rise of temperature.[1]

(8) The application of an approximate correction for the unimmersed part of the stem.

It should be noticed that the resulting degrees obtained by a mercury thermometer correspond to equal increments of volume of mercury when heated. In other words, if one cubic cm. of mercury at the temperature of melting ice become equal to $(1 + a)$ cc.s. when the temperature is raised to that of water boiling under standard conditions, then the temperature corresponding to a volume of the same mercury equal to $1 + x$ will be equal to $\frac{100x^\circ}{a}$ C., on the mercury thermometer scale.

QUESTIONS

(1) Mercurial thermometers are now issued with corrections stated to 0·001° C. State exactly what precautions are taken in the manufacture and use of the thermometers to make it possible to aim at this degree of accuracy.

(2) Describe the principal errors of the mercurial thermometer and the means used to reduce them.

(3) Explain the meaning of the term "Standard atmosphere." What observations would you make to determine the atmospheric pressure at a given place?

(4) Describe how an accurate barometer is constructed, and explain how to correct its readings so as to determine the pressure of the air.

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[1] A falling temperature cannot be accurately determined by the aid of a mercury thermometer (Griffiths).

(5) Describe the difficulties in the way of accurate thermometry by means of mercury thermometers, and the precautions that must be taken in order to obtain accurate results, say to 0·01° C. in making measurements of change of temperature in calorimetry.

(6) On a certain day the pressure, as read from a Fortin's barometer, was 75·29 cms. and the temperature was 18° C. At what temperature would water boil on that day?

CHAPTER III

EXPANSION OF SOLIDS

THE dimensions of all bodies are altered more or less by an increase or decrease in temperature. Solid bodies have the property of retaining their shape without the support of a containing vessel. Hence in the case of a solid bar we may measure the increase in length, breadth, or thickness due to a given rise of temperature, and thus determine the **increase in length which a bar of 1 cm. long would experience if heated through 1° C.** This is defined as the **coefficient of linear expansion of the substance of which the bar is composed.**

On the other hand, fluids take their shape from the vessel in which they happen to be contained. It would therefore obviously be useless to make measurements of the linear dimensions of a fluid, unless to obtain its volume. A certain mass of water, for instance, may be poured into vessels of various shapes and sizes, its linear dimensions being thus capable of modification in an infinite number of ways. But through all these modifications the volume of the water will remain the same, providing its temperature is not altered; whilst every alteration in temperature of the water will produce a corresponding alteration in its volume. Hence it is rational to confine our attention, in the case of a fluid, to the alteration in volume which accompanies an increase in temperature.

Fluids are divided into liquids and gases. The volume of a gas is altered, not only by an increase or decrease of temperature, but also, and to an equal extent, by changes of pressure.

The contraction which occurs when a metallic body is cooled is frequently utilised by engineers. A good example is afforded in the manufacture of large cannon. The general shape of one of these is shown in the sectional drawing (Fig. 18). An inner tube of steel is first turned accurately cylindrical on the outside, and bored internally. This tube, though sufficiently strong to guide the projectile in a straight course, is not strong enough to withstand the great force suddenly called into play by the explosion of the powder. To furnish sufficient strength a number of steel coatings are successively shrunk on to the tube. Each of these coatings is bored internally to such a diameter that, when at the same temperature as the rest of the cannon, it is too small to fit in place. On being heated, however, (the rest of the cannon remaining cold) it just slips into position, and when cooled is held tightly there.

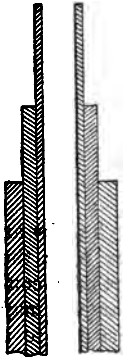

FIG. 18.—Section of Cannon.

EXPT. 11.—The enormous force called into play when the expansion of a metal rod is resisted by mechanical means is illustrated in the following experiment. A rod of steel or wrought iron is provided, at one end, with a nut which can be screwed on to it, and at the other with a hole through which a small bar of cast iron can be placed. A strong metal stand is furnished with two upright pillars, provided at their upper extremities with knife edges against which the cast-iron bar and the nut can respectively rest. The nut is screwed up tightly so as to put some compressional strain on the bar. If the latter be now heated, the force called into play will be sufficient to break the cast-iron bat.

A simple modification of this experiment shows that an equally great force is called into play when the contraction, due to cooling a heated rod, is resisted by mechanical means.

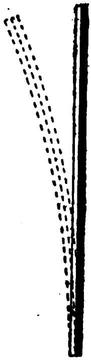

FIG. 19.—Compound strip, showing differential expansion.

EXPT. 12.—Take a strip of ebonite, about a foot long and an inch broad, and as thin as can be procured, and glue this on to a strip of wood (pine by preference) of similar dimensions, so that the two form a compound strip of double the thickness of the wood or the ebonite. (A thin strip of wood such as here required can be easily obtained by the use of a circular saw.) If this compound strip, Fig. 19, be heated, it will be found to bend into a curve such as shown by the dotted lines. The reason of this is, that the increase in length of a strip of ebonite is greater than that of a similar strip of wood when both are subjected to the same rise of temperature. The compound strip can only remain straight when both of its components are of equal length; if the length of one component becomes greater than that of the other, the compound strip will assume a curved form, with the longer strip on the convex side of the curve.

Strips of brass and steel may be substituted for the ebonite and wood, when it will be found that for a given rise of temperature brass expands more than steel.

Expt. 13.—Take about a foot of indiarubber pressure tubing (the kind containing an internal layer of canvas is unsuitable), and fix a small piece of open glass tube into one end, a small wooden rod being placed in the other end. Bind both in position by means of thin copper wire. A loop of copper wire is attached to the glass tube, and

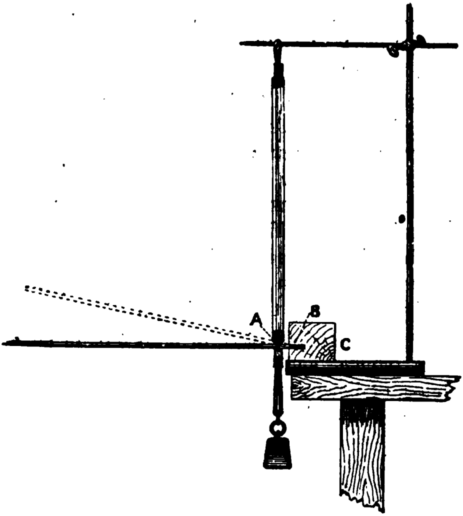

Fig. 20.—Arrangement for showing the effect of heating on stretched india-rubber.

another to the wooden rod. A fine sewing needle is driven through the wooden rod at right angles to its length, and a mass of about a pound having been hung from the loop at this end of the tube, the other end is attached to a horizontal arm of a retort stand, Fig. 20. A straw has two holes burnt through it at right angles to its length by means of a hot needle, the distance between the holes being about a quarter of an inch. The needle A, projecting through the wooden rod at the lower extremity of the indiarubber tube, is placed through that hole in the straw which is nearest to the centre of the latter. Another needle B, driven into a block of wood C, is placed in the other hole in the straw, and the whole is adjusted so that the straw is horizontal.

If the indiarubber tube is now heated by the flame of a Bunsen burner, the straw will indicate that a contraction takes place in the indiarubber.

It must not, however, be concluded from this experiment that indiarubber contracts when heated. As a matter of fact, if a mass is employed only just sufficient to keep the tube straight without stretching it, it will be found that the indiarubber expands when heated.

The legitimate conclusion to be drawn from this experiment is that *though indiarubber expands when heated, a given stretching force will produce a smaller extension when the temperature is high than when it is low.*

Coefficient of Linear Expansion of a Metal.—In order to determine the coefficient of linear expansion of a metal, the usual method is to observe the elongation produced by a given rise of temperature in a bar of known length. The chief difficulty lies in measuring the small elongation.

EXPT. 14.—Take a straight piece of brass tube of circular section, of length about 120 cm., and diameter about 2 cm. Take two pieces of flat sheet brass, of dimensions about 5 cm. × 2 cm. × ·3 c.m. These two pieces must be soldered, one at each end, to the curved surface of the brass tube, so that they lie in one plane, a part of each projecting beyond the end of the tube. This may easily be done by placing the two pieces of brass on a flat table, laying the brass tube upon them, and effecting the soldering by means of a bit and the ordinary flux (zinc chloride solution.) Blanks must be soldered into the ends of the tube, and two side tubes, C, D, (Fig. 21) also soldered in position, so that water or steam may be passed through them.

The arrangement to be made may be understood from Fig. 21. AB represents the tube, with the side tubes C, D, and the brass plates E, F. E is placed on a block of wood, and held in position by means of a weight W_1. F rests on a needle N, which in turn rests on a piece of flat glass supported on a block of appropriate height. The needle N has one end inserted at right angles into a counterbalanced straw P, which is to serve as a pointer. The needle may be fixed tightly to the straw by means of a little sealing wax. A weight W_2 serves to press the brass plate F on to the needle.

On starting the experiment, arrange the pointer P so that it is vertical, and points to 0° on the circular scale graduated in degrees. Observe the temperature of the room $(t_0\ \mathrm{C})^\circ$.

Now pass steam through the tube AB by means of india-rubber tubes joined to C and D; that joined to C being connected at its other end with a piece of glass tube thrust through the cork in the mouth of a tin can in which water is boiled. As the tube AB is heated it will increase in length, and the end A being fixed, the end B will roll on the needle N and thus cause the pointer P to revolve.

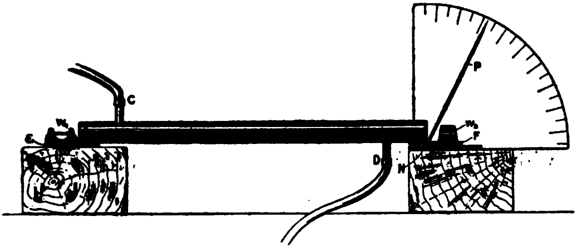

FIG. 21.—Arrangement for measuring the expansion of a metal tube.

Let us suppose that when steam has passed freely through AB for ten minutes or so, it is found that the pointer indicates θ°. Further, let d = the diameter (in cms.) of the needle, as measured by a micrometer gauge.

Now for a complete rotation of the needle (*i.e.*, through 360°), the needle will advance through πd cms. and the end of the brass tube will advance through twice this distance. Therefore for a rotation through θ°, the end of the tube would advance through

$$2\pi d \times \frac{\theta}{360}\ \text{cms.}$$

Let L = the length of the tube, and $(100 - t_0)^\circ$ = the increase in its temperature. Then,

A length L of brass, when heated through $(100 - t_0)^\circ$ C., is increased in length by $\frac{d\pi\theta}{180}$ cms.

∴ Unit length of brass, when heated through 1° C., is increased in length by $\frac{d\pi\theta}{180\,L\,(100 - t_0)}$.

Accurate results may be obtained by the aid of the arrangement just described. If the outside of the brass tube is enveloped in cotton wool, a slight advantage is gained, otherwise the outside of the tube is slightly colder than the inside.

The accuracy of this and similar methods depends on no expansion having taken place in the table or bench on which the supporting blocks rest. A little care will ensure that this condition is complied with. The reason why the absolute expansion of a metal cannot be directly obtained by a modification of the above method, supporting a bar on two metallic blocks fastened to the bottom of a metallic trough which can be filled with water at any required temperature, is obvious. In this case the relative expansion of the metals composing the bar and the trough may be obtained, and if the coefficient of expansion of one of these is known, that of the other may be calculated.

Weedon's Expansion Apparatus.—Mr. Weedon has recently invented a laboratory apparatus which can be used successively with a number of different metal bars. It consists of a long zinc trough, in which is placed the rod, one metre long, the expansion of which is to be measured. A burner is supported underneath the trough, running the whole length of it, and provided with a double set of holes and two inlet gas pipes, so that the water contained in the trough may be heated to boiling point. The ends of the trough have stuffing boxes, through which pass short glass rods, abutting on the one side against the ends of the metal rod, and on the other against two delicate micrometer gauges which are supported in two firm cast-brass clamps fixed to solid teak blocks. A metal screen at each end, faced inside with asbestos, prevents heat from radiating to the micrometer gauges, thus eliminating errors due to the expansion of the screws. The supports for the trough, burner, &c., are placed in a cold-water trough, provided with inlet and exit pipes, and running the whole length of the base. The cold-water bath thus prevents any expansion of the base and supports due to heat radiated from the burner and the hot-water trough above.

The method of working the apparatus is as follows: the micrometers having been screwed back sufficiently far to permit of the maximum expansion of the bar, the burner is lighted and the water in the upper trough raised to as near boiling point as possible. When this maximum temperature is attained, one micrometer is screwed in until the screw comes in touch with the short glass end-pieces. The other micrometer is now screwed up very carefully until it is felt to just grip the metal bar. The readings of both micrometers must be taken. The gas burners are now lowered, so that the temperature of the water in the trough may become lower, when another observation may be made. Readings may be taken for differences of 10° C. from 100° to 20°.

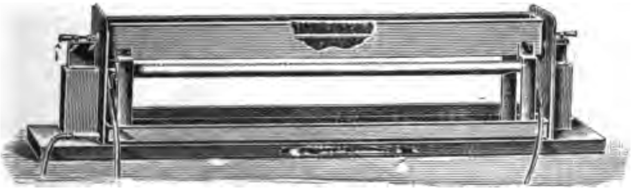

FIG. 22.—Weedon's Expansion Apparatus.

Let L be the length of the metal rod, and l be its elongation, due to a rise of temperature of $t°$. Then

Coefficient of linear expansion of rod = elongation per degree Centigrade of 1 cm. length of rod $= \frac{l}{Lt}$.

This apparatus would be just as efficacious, and certainly less costly, if provided with only one micrometer gauge, a fixed stop being substituted for the other.

Roy and Ramsden's Method.—In order to accurately determine the expansion of the bars used by General Roy in when both bars are placed in a bath, which is heated successively to two observed temperatures, will give the difference of the expansions of the bars. By this means Dulong and Petit determined the relative expansion of several metals with regard to platinum, and the absolute expansion of the latter metal having been determined, the coefficients of expansion of the other metals were calculated.

Measurements of the relative expansion of two bars of different metals, made with an apparatus similar to the above, might obviously be utilised for the determination of high temperatures, just as the relative expansion of mercury and glass is used in an ordinary thermometer.

Non-Expansible Alloy.—M. Guillaume[1] has found that an alloy of steel containing 36 per cent. of nickel has an exceedingly small coefficient of linear expansion, amounting to no more than one-tenth of that of platinum. Its actual value is about $8{\cdot}7 \times 10^{-7}$. Thus a rod of nickel steel of the above composition, a metre long, when heated through 100° C., would be increased in length only by $100 \times 100 \times 8{\cdot}7 \times 10^{-7} = 8{\cdot}7 \times 10^{-3}$ cm., that is, by a little less than a tenth of a millimetre. On the other hand, since the coefficient of linear expansion of brass is equal to about $1{\cdot}9 \times 10^{-5}$, a brass bar a metre long, when heated through 100° C., would increase in length by $100 \times 100 \times 1{\cdot}9 \times 10^{-5} = 1{\cdot}9 \times 10^{-1}$ cm., that is, by a little less than two millimetres. Nickel steel is not readily rusted by moist air or water. Further, the full expansion for nickel steel is only obtained after several days heating; indeed, when the increase of temperature is small, the increase in length does not attain its maximum value (*i.e.*, that calculated from the coefficient of expansion given above) for the space of two months. Hence, when a bar of Guillaume's nickel steel is subjected only to fluctuations of temperature which are neither very far removed from the mean temperature of the bar, nor very long in duration, the length of the bar may be considered to remain constant. This property should render Guillaume's nickel steel particularly suitable for the construction of pendulums, &c.

Example 1.—A seconds pendulum is composed of a small sphere of platinum attached to the end of a very thin rod of brass. It beats seconds accurately at 0° C.; if the pendulum is kept at a temperature of 10° C., how many seconds will be lost in a week?

---

[1] *Comptes Rendus*, 124, p. 176–9 and 752–5, 1897.

(Coefficient of linear expansion of brass = $1\cdot9 \times 10^{-5}$.)

One complete oscillation (to and fro) of a seconds pendulum occupies 2 seconds. If t is the time occupied by a complete oscillation of a simple pendulum of length l, then

$$t = 2\pi\sqrt{\frac{l}{g}}$$

where g = the acceleration due to gravity. (= 981 cm./sec^2.)

Let us suppose that the length of the pendulum, at 0° C., is equal to l cm. Now a length of 1 cm. of brass, when heated through 1° C., would be increased to $(1 + \cdot000019)$ cm.; if heated through $t°$ C., it would possess a length of $(1 + \cdot000019 \times t)$ cm. Further, if a length of l cms. were in question, since each centimetre would expand by the above amount, the length of the whole bar at $t°$ C. would be equal to

$$l(1 + \cdot000019t°).$$

Number of complete oscillations made by pendulum in a week, the temperature being 0° C.,

$$= \tfrac{1}{2} \times 60 \times 60 \times 24 \times 7 = 302{,}400.$$

At 10° C. the number of complete vibrations in a week will be equal to

$$\frac{\text{Number of seconds in a week}}{\text{Time occupied by a complete vibration}} = \frac{60 \times 60 \times 24 \times 7}{2\pi}\sqrt{\frac{g}{l(1 + \cdot000019 \times 10)}}$$

$$= \frac{302{,}400}{\pi}\sqrt{\frac{g}{l(1+\cdot00019)}} = \frac{302{,}400}{\pi}\sqrt{\frac{g}{l}}\sqrt{\frac{1}{1+\cdot00019}}$$

Also since $t = 2$ for a seconds pendulum,

$$2 = 2\pi\sqrt{\frac{l}{g}} \text{ at } 0° \text{ C.}$$

$$\therefore \frac{1}{\pi}\sqrt{\frac{g}{l}} = 1.$$

∴ Number of vibrations performed a week, when the temp. is 10° C.

$$= 302{,}400\sqrt{\frac{1}{1\cdot00019}}$$

Further,

$$\sqrt{\frac{1}{(1+a)}} = \frac{1}{(1+a)^{\frac{1}{2}}} = 1 - \tfrac{1}{2}a + \tfrac{3}{8}a^2 - \tfrac{5}{16}a^3 + \ldots\ldots$$

(This result, with which the student should make himself thoroughly acquainted, may be deduced from the binomial theorem, or obtained by ordinary algebraical operations.)

$$\therefore \sqrt{\frac{1}{1+\cdot 00019}} = 1 - \tfrac{1}{2} \times \cdot 00019 + \tfrac{3}{8}(\cdot 00019)^2 - \tfrac{5}{16}(\cdot 00019)^3 + \ldots$$
$$= 1 - \cdot 000095 + \cdot 0000000135 - \ldots\ldots\ldots$$

It will at once be seen that the third and all succeeding terms are very small in comparison with the second, and may therefore be neglected. Consequently, number of vibrations completed in a week, at a temp. of 10° C.,

$$= 302{,}400\,(1 - \cdot 000095).$$

Number of vibrations completed in a week, at 0° C. = 302,400.

∴ Number of vibrations lost in a week, when the temperature of the pendulum is kept at 10° C.,

$$= 302{,}400 \times \cdot 000095 = 28\cdot 7.$$

∴ Number of seconds lost = 57·4.

Example. The definition of the coefficient of linear expansion, given at the commencement of the present chapter, is couched in terms of the centimetre and Centigrade degree as units. What alteration would have to be made in its value (1) taking the foot and Centigrade degree as units; (2) taking the foot and Fahrenheit degree as units?

(1) (1 inch = 2·54 cm.)

Let a = the coefficient of expansion of a substance, as defined at the commencement of this chapter. Then a bar 1 cm. long of the substance under consideration, when heated through 1° C., will be increased in length by a cm.

Hence a bar of the same substance 1 ft. long would be increased in length by $12 \times 2\cdot 54 \times a$ cm. Converting this to feet, we find that a bar 1 ft. long would, when heated through 1° C., be increased in length by

$$\frac{12 \times 2\cdot 54 \times a}{12 \times 2\cdot 54} = a \text{ ft.}$$

Hence the value of the coefficient of Linear Expansion of a body is independent of the unit of length used.

(2) $1^\circ \text{F} = \left(\frac{5}{9}\right)^\circ \text{C}.$

Consequently, if we define the coefficient of linear expansion in terms of the degree Fahrenheit, since the latter is smaller than the degree Centigrade, the increase in length of a bar of unit length when heated through 1° F. will be $\frac{5}{9}$ of the increase in length when the same bar is heated through 1° C.

The most general definition of the coefficient of Linear Expansion of a substance is the increase in length of a bar of unit length, when heated through unit difference of temperature.

Example. Steam pipes, which are sometimes allowed to cool, must be provided with unions allowing expansion and contraction to take place. How much play must be allowed at each union, supposing each separate pipe to be 6 ft. long?

Coefficient of linear expansion of iron = ·000012 per degree Centigrade. Lowest temperature of pipes = 0° C.

A pipe 6 ft. long at 0° C. will become

$$(1 + \cdot000012 \times 100) \times 6 \text{ ft.} = 1\cdot0012 \times 6 \text{ ft. long at } 100^\circ \text{ C.}$$

Hence maximum expansion = ·0072 ft. = ·0864 inch.

Hence about a tenth of an inch play must be allowed at each joint.

Example. When a house, in the construction of which iron girders have been used, is burnt down, the girders are generally found to have been greatly bent. Assuming that this is due to the fact that one side of the girder has been heated to a higher temperature than the other, what curvature might we expect in an H girder, the distance between two parallel sides of which is 6 inches, assuming that the highest difference of temperature likely to exist between the latter is 500° C.?

For a first approximation we may assume that the girder is bent into an arc of a circle. Let θ be the angle subtended at the centre by this arc, and R be the radius of the circle in inches. (Fig. 25.)

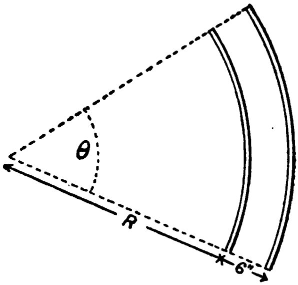

FIG. 25.—Iron girder heated on one side.

The length of the cold (concave) side of girder = $R\theta$.
" " hot (convex) " = $(R + 6)\theta$.

But, since the coefficient of linear expansion of iron is about ·000012, we have the relation

$$\frac{\text{Length of hot side of girder}}{\text{Length of cold side of girder}} = \frac{1 + \cdot000012 \times 500}{1}$$
$$= 1\cdot006.$$

$$\therefore \frac{(R+6)\theta}{R\theta} = \frac{R+6}{R} = 1\cdot006.$$

$$\therefore R \times \cdot006 = 6. \quad R = 1{,}000 \text{ ins.} = 83\tfrac{1}{3} \text{ ft.}$$

With narrower girders, of course, a greater bending would result.

Example. A metallic sheet is 50 cm. long and 20 cm. wide at 0° C. If it is heated to 60° C., what will be its increase of area?

$$\text{Original area} = 50 \times 20 = 1{,}000 \text{ cm.}$$

Let a = the coefficient of linear expansion of the metal.

$$\text{Then length of sheet at } 60^\circ \text{ C.} = 50(1 + 60a).$$
$$\text{Width} \ldots\ldots\ldots\ldots = 20(1 + 60a).$$
$$\therefore \text{Area of sheet at } 60^\circ \text{ C.} \ldots = 1{,}000(1 + 60a)^2.$$
$$= 1{,}000(1 + 2 \times 60a + (60a)^2)$$

The term $(60a)^2$ will be very small, and may therefore be neglected. Hence

$$\text{Area of sheet at } 60^\circ \text{ C.} = 1{,}000(1 + 2 \times 60a).$$

By a similar process of reasoning, it can be shown that a metallic sheet exactly 1 cm. sq. at 0° C., of which the coefficient of linear expansion is a, will possess an area of $(1 + 2a)$ sq. cm. at 1°, and $(1 + 2at)$ sq. cm. at t°. The quantity $2a$ is defined as the coefficient of superficial expansion of the metal.

The coefficient of Superficial Expansion of a substance represents the alteration in area of a sheet of the substance initially possessing unit area, when it is heated through unit difference of temperature.—Its numerical value, from the above, is equal to twice the coefficient of linear expansion of the substance in question.

TABLE OF LINEAR EXPANSION OF SOME SUBSTANCES.

Fused quartz	0·0000007
Steel alloyed with 36% nickel	0·00000087
Glass (tube)	0·00000833
Platinum	0·00000899
Iron (soft)	0·0000121
Gold	0·0000144
Copper	0·0000168
Brass	0·000019
Zinc	0·0000292

Expansions of Glass and Platinum.—It may be noticed that the coefficients of linear expansion of glass and platinum are nearly equal. This makes it possible to seal a platinum wire directly into a glass tube or bulb, and thus renders the manufacture of electric glow lamps possible. When hot, the melted glass adheres to the hot platinum wire, and as both contract at nearly the same rate on cooling, no strain is produced in the glass. It is possible, though not always very easy, to seal a thin iron wire into glass, provided that it is arranged that cooling takes place gradually.

Compensated Pendulums.—The time t occupied by a complete (to and fro) oscillation of a pendulum is given by the equation

$$t = 2\pi \sqrt{\frac{l}{g}},$$

where l = length of pendulum,
g = acceleration due to gravity.

Hence, any cause which increases the length of a pendulum will also increase the time occupied by one of its oscillations.

If a pendulum is formed from a heavy mass attached to the end of a metal rod, since the length of the rod will be greater at high than at low temperatures, one oscillation will occupy a greater time on a hot than on a cold day. If the pendulum is used to control the working of a clock, the latter will gain in cold, and lose in hot weather. In order to prevent this, several different methods have been proposed.

Fig. 26, A, shows one of the simplest forms of a compensated pendulum, which is nevertheless very satisfactory in its behaviour. The rod of the pendulum is made of well-seasoned wood. A cylindrical zinc bob is bored to slip loosely on the rod, and is supported from its lower surface by means of a nut fitted to a brass screw attached to the extremity of the wooden rod. Now if the zinc alone were heated, it would expand in all directions, and consequently become longer. As the lower end of the cylinder is maintained always at the extremity of the wooden rod, any lengthening of the cylinder will cause the centre of gravity of the latter to reach a higher position along the wooden rod. If now the zinc cylinder is made of such a length that the ascent of its centre of gravity due to a given rise of temperature is just equal to the lengthening of the wooden rod from the same cause, the distance of the centre of gravity of the bob from the point of suspension will remain constant, and the pendulum will oscillate approximately at the same rate whatever the temperature of the surrounding air may be.

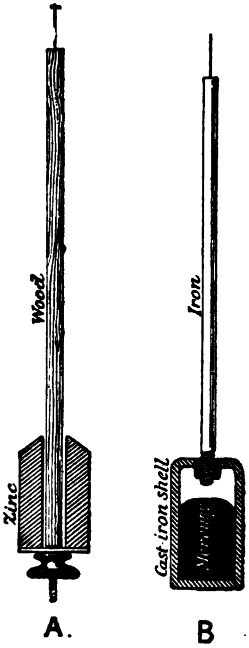

FIG. 26.—Compensated Pendulums.

Fig. 26, B, shows a similar but more effective form of compensated pendulum, due to Graham. A cast-iron cylinder is screwed on to the end of an iron rod ; this cylinder contains such a quantity of mercury that its expansion for any rise of temperature will give rise to an ascent of its centre of gravity, which will just counterbalance the extension of the iron rod due to the same rise of temperature.

An approximate calculation may be made as to the height to which mercury must be poured into the cistern in order that a compensation may be effected. Assuming (what is, however, not strictly correct) that the coefficient of linear expansion of the iron composing both rod and cistern is equal to ·000012, whilst the coefficient of absolute cubical expansion of mercury is ·000180, we may proceed as follows. Let $l =$ the distance from the free end of the rod to the bottom of the cistern, and let h_0 = the height of the mercury in the cistern, at 0° C. If the rod and cistern possess small masses compared with that of the mercury used, the centre of gravity of the whole pendulum may be taken as coinciding with that of the mercury. Hence the approximate length of the equivalent simple pendulum at 0° C. $= l - \frac{h_0}{2}$.

Now let a rise in temperature of t° C. take place. If V = the total volume of mercury, and S is the sectional area of the cistern, at 0° C., then

$$\frac{V}{S} = h_0 \text{ at the initial temperature.}$$

After the rise of temperature, we shall have

$$h_t = \frac{V(1 + \cdot 000180 \times t)}{S(1 + 2 \times \cdot 000012 \times t)}$$

since S represents a superficial area, and hence the coefficient of superficial expansion (equal to twice the coefficient of linear expansion) of the iron must be used. (*See* Example 5). Hence, expanding by the binomial theorem, we have

$$\begin{aligned} h_t &= \frac{V}{S}(1 + \cdot 000180t)(1 - \cdot 000024t + \ldots\ldots) \\ &= \frac{V}{S}\{1 + (\cdot 000180 - \cdot 000024)t + \ldots\} \\ &= \frac{V}{S}(1 + \cdot 000156t). \end{aligned}$$

Also the length l will be increased, due to the same rise of temperature, to $l(1 + \cdot 000012\, t)$.

Finally, in order that the length of the equivalent simple pendulum should remain unaffected by temperature, we have

$$l - \frac{h_0}{2} = l(1 + \cdot 000012\, t) - \tfrac{1}{2}\frac{V}{S}(1 + \cdot 000156\, t).$$

Remembering that $\frac{V}{S} = h_0$, we have

$$\cdot 000012 \times lt = \frac{\cdot 00015}{2} \cdot \frac{V}{S}\, t.$$

$$\therefore \frac{V}{S} = 2 \times \frac{\cdot 000012}{\cdot 00015}\, l,$$

$$\text{and } h_0 = \frac{\cdot 000024}{\cdot 00015}\, l.$$

that is, the height of the mercury in the cistern must be about ·16 of the total length of the pendulum.

Perhaps the most common form of compensated pendulum is that shown in Fig. 27, and known as Harrison's Gridiron Pendulum. Referring to the table on p. 53, it will be seen that the coefficient of linear expansion of brass is about 1½ times that of iron. Hence, since the elongation of a rod when heated through a certain number of degrees is proportional both to its coefficient of linear expansion and its length, it follows that if an iron rod is heated, it will be elongated by the same amount as a brass rod of ⅔rds its length, the rise in temperature being the same in both cases. Hence if, in Fig. 28, AB and CD represent two rods of iron and brass respectively, CD being ⅔rds of AB, then the point D will remain stationary to whatever temperature the two bars may be heated. Hence, if a massive sphere S be fastened to the end of D, its centre will always remain at the same distance from E, the point of suspension;

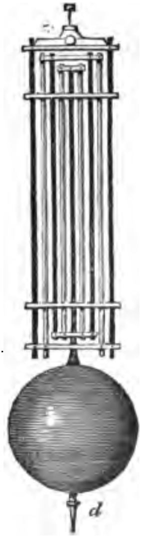

FIG. 27.—Harrison's Compensated Pendulum.

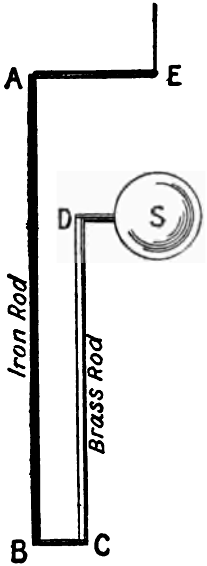

FIG. 28.—Principle of Compensated Pendulum.

and if we may assume the centre of gravity of the whole pendulum to coincide approximately with the centre of the sphere, the length of the equivalent simple pendulum will remain unaffected by temperature changes.

This form of pendulum would, however, be very awkward to use, owing to its excessive length. The arrangement shown in Fig. 27 is that generally employed. The black bars are of iron, the unshaded ones of brass. The two middle cross bars only act as guides, being drilled with holes through which the rods fit loosely. The expansion of each iron rod tends to lower the pendulum bob, whilst that of each brass rod tends to raise it. Since the total length of the three iron rods is about 1½ times that of the two brass rods found on one side of the pendulum, the position of the bob relatively to the point of suspension, is independent of the temperature of the pendulum.

A similar, but simpler construction has been used for the pendulum of the large clock above the Houses of Parliament, Westminster. Here an iron rod C is surrounded by and attached at one end to the extremity of a zinc tube B (Fig. 29). The upper extremity of this zinc tube is attached to the end of an iron tube A which surrounds it, the bob being attached in its turn to the lower end of this iron tube. Hence the expansion of the iron tends to lower the bob, whilst the expansion of the zinc tends to raise it. The coefficient of expansion of zinc is about 2½ times that of iron; hence the combined length of the iron rod and the outer iron tube being made 2½ times that of the zinc tube, the centre of gravity of the bob remains always in the same position, whatever may be the temperature.

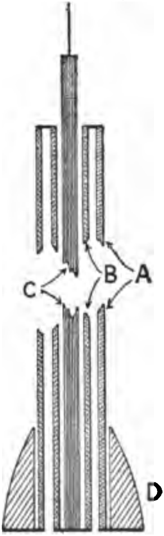

FIG. 29.—Compensated Pendulum.

Ventilation holes are provided in both tubes, so that the whole of the pendulum may be capable of quickly attaining the same temperature.

Compensated Balance Wheels.—An uncompensated balance wheel of a watch will oscillate at different rates at different temperatures. This is due to the fact that the mean distance of the metal in the rim from the centre of rotation is increased when the wheel is heated, whilst the elasticity of the spring is also affected by a change of temperature. To obtain a balance wheel which will oscillate at the same rate whatever the temperature may be, the rim is made in three pieces; each is fastened at one end to one of the spokes, and carries a weight near its other extremity, which is left free. Each section of the rim is composed of two strips of metal lying one outside the other, the outer strip being composed of a more expansible metal than the inner strip. When the wheel is heated, the following alterations will occur:—

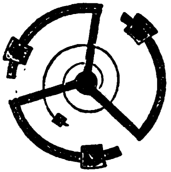

FIG. 30.—Compensated Balance Wheel.

(1) The spokes will be lengthened; this alone would tend to remove the weights on the rim farther from the centre of rotation.

(2) Owing to the fact that the rim is composed of two strips fastened together, the outer being the more expansible, heating the wheel will tend to increase the curvature of the sections of the rim, thus bringing the weights nearer to the centre of curvature.

When a suitable adjustment has been made, the balance wheel will oscillate at the same rate whatever the temperature may be.

It is well to remember, however, that the mere fact that a watch is provided with a compensated balance wheel is of no advantage, unless a proper adjustment has been made.

In laying rails for railways, in building iron bridges, and in all operations where large masses of metal may be subjected to variations of temperature, allowance for expansion must be made. Some examples illustrating this will be found at the end of this chapter.

Cubical Expansion.—When a solid body is heated, each of its linear dimensions is altered, and consequently the total volume of the body is changed. In some substances, such as glass and metals generally, the various dimensions are altered in the same proportion. Thus, if a metallic rod of rectangular section be heated, its length, breadth, and thickness will be increased in the same proportion.

Let L = the length of the rod.
B = „ breadth „
D = „ thickness „

The initial volume = V = L B D.

If the coefficient of linear expansion of the substance of which the rod is composed be denoted by a, whilst the rise in temperature is denoted by t, then

$$\begin{aligned} \text{Length at higher temperature} &= L(1 + at) \\ \text{Breadth} \ldots\ldots\ldots\ldots &= B(1 + at) \\ \text{Thickness} \ldots\ldots\ldots\ldots &= D(1 + at). \\ \therefore \text{Volume at higher temperature} &= L\,B\,D\,(1 + at)^3. \\ &= V(1 + at)^3. \end{aligned}$$

If L, B, and D be each equal to 1 cm., then we have

Increase in volume of 1 c.c. of the substance, due to heating through

$$\begin{aligned} t^\circ \text{C.}, = (1 + at)^3 - 1 &= (1 + 3\,at + 3\,a^2t^2 + a^3t^3) - 1 \\ &= 3\,at + 3\,a^2t^2 + a^3t^3. \end{aligned}$$

In accordance with reasoning previously explained, terms involving powers of a higher than the first may be neglected. Hence—

Increase in volume of 1 c.c. of the substance when heated through t° C. = $3at$.

∴ Increase in volume of 1 c.c. of substance when heated through 1° C = $3a$ = three times the coefficient of linear expansion.

The increase in volume of unit volume of a substance due to heating it through unit difference of temperature, is called the coefficient of cubical expansion of the substance.—Its numerical value, for a substance which expands equally in all directions, is equal to three times the coefficient of linear expansion of the substance. The numerical value is independent of the unit of length chosen, but will vary with the thermometric scale used (*see* p. 51).

A body which has similar properties in all directions about any point in it is said to be isotropic.

Some substances, such, for instance, as crystals, &c., have different properties in different directions. To take a familiar instance, the coefficient of linear expansion of wood has a different value perpendicular to the grain from what it has parallel to the grain. Such substances are said to be **æolotropic.**

Certain crystals have different coefficients of expansion in three rectangular directions. Let us suppose that a unit cube is cut from such a crystal, the sides of the cube being respectively parallel to the three rectangular directions or axes which possess the most divergent coefficients of expansion. Let the value of these coefficients be taken as α_1, α_2, α_3.

The increase in volume of the unit cube when heated through $1^\circ C = (1 + \alpha_1)(1 + \alpha_2)(1 + \alpha_3) - 1$

$$= (\alpha_1 + \alpha_2 + \alpha_3) + (\alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1) + \alpha_1\alpha_2\alpha_3.$$

The terms $(\alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1)$ and $\alpha_1\alpha_2\alpha_3$, both of which involve the *products of small quantities*, may be neglected. Hence

Coefficient of expansion of an æolotropic substance
$= \alpha_1 + \alpha_2 + \alpha_3 =$ the sum of the principal coefficients of linear expansion.

Expansion of Crystals.—In order to determine the coefficients of linear expansion of a crystal, M. Fizeau has used the following arrangement.

A small metal table AB is supported by means of three levelling screws. On the upper projecting extremities of the levelling screws rests a small plate of optically worked glass CD.

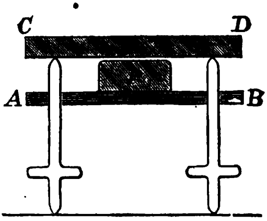

FIG. 31.—Fizeau's Optical Interference Method of Determining Expansion. (P.)

The crystal to be examined is ground so as to have two parallel surfaces perpendicular to the axis along which it is required to measure the expansion. This crystal P is placed on the metal table AB, and the position of the plate CD is adjusted so that it lies very nearly parallel to, and at a small distance from, the upper surface of the crystal P. When this adjustment has been correctly performed, if the air film contained between CD and P is illuminated by means of light from a sodium flame, alternate bright and dark bands will be seen on looking vertically downwards at P. These bands are similar to those formed when two suitable lenses are pressed together, *i.e.*, to Newton's Rings. If the distance between the upper surface of P and the lower surface of CD is varied, a movement will be produced in these bands. Consequently if the stand and the plate, &c., which it supports are heated, an observation of the motion of the bands will suffice to determine the difference between the expansions of the crystal and of the parts of the levelling screws projecting above AB.

Mr. A. E. Tutton has lately improved this apparatus by supporting the crystal on a small three-legged table made of aluminium, which rests on the upper surface of AB, the levelling screws being made of platinum. The relative height of the aluminium table and the parts of the levelling screws projecting above AB are so arranged that the upward motion of the crystal due to the expansion of the aluminium is just equal to the increase in distance between AB and CD, due to the expansion of the platinum. Thus the expansion of the platinum screws is compensated for, and the absolute expansion of the crystal is directly determined.

SUMMARY.

The linear dimensions of solids are altered by a change of temperature.

The Coefficient of Linear Expansion of a solid is defined as the increase in length of unit length of the solid when the temperature is raised by one degreee.

One of the earliest, and at the same time one of the best, methods of measuring the expansion of a rod of metal is that due to Ramsden. Eyepieces and object glasses were arranged so as to constitute two microscopes. The object glasses were displaced by the expanding bar, and the elongation was calculated from an observation of the relative displacement of the images of two sets of stationary cross-wires.

When the true coefficient of expansion of a single metal is known, the coefficients for other metals may be determined by a method similar to that described on p. 47.

Superficial Expansion.—The coefficient of superficial expansion of an isotropic solid is equal to twice the coefficient of linear expansion of the solid.

Cubical Expansion.—The coefficient of cubical expansion of an isotropic solid is equal to three times its coefficient of linear expansion.

Pendulums.—Since the length of an uncompensated pendulum will be greater in hot than in cold weather, a clock controlled by such a pendulum will lose in hot weather and gain in cold weather. To avoid this, *compensated pendulums* are used. In these, the centre of gravity of the pendulum bob is maintained at a uniform distance from the point of suspension, by using two or more different metals in its construction. The expansion of one metal, tending to lengthen the pendulum, is compensated by the expansion of the other metal, which tends to shorten the pendulum.

Balance wheels of watches are compensated by arranging that masses of metal carried by the rims of the wheel are maintained at a uniform distance from the centre of rotation, whatever the temperature may be. In actual practice, the compensation is adjusted to correct for temperature alterations in the elasticity of the hair spring, as well as expansions of the balance wheel.

In all large metal structures, such as bridges, &c., arrangements must be made to allow expansions and contractions to occur.

Expansion of Crystals.—A crystal expands by different amounts in different directions.

The coefficient of cubical expansion of a crystal is equal to the sum of the three principal coefficients of linear expansion of the crystal.

Fizeau employed a delicate optical method to determine the expansion of a crystal. Interference fringes were produced between one face of the crystal and a glass plate. An observation of the displacement of the fringes gave the expansion of the crystal in terms of the wave length of the light used.

QUESTIONS ON CHAPTER III.

(1) Give an account of an accurate method of determining the coefficient of linear expansion of a solid.

(2) Explain how the length expansion of a rod with rise of temperature may be accurately measured.

(3) A steel metre scale is correct at 0° C. What correction must be applied to a length equal to 79·512 cms., measured by means of the above scale at a temperature of 30° C.?

(4) Describe and explain the Gridiron pendulum.

(5) Define the coefficient of linear expansion of a solid, and describe an *accurate* method of determining it.

Two copper bars, each 30 cms. long at 0° C., are placed in one straight line, with their outer ends fixed. Find how far their inner ends must be apart so that they may just touch at a temperature of 50° C. (coefficient of linear expansion of copper 0·000017).

(6) Assuming that the highest summer temperature is 45° C., and the lowest winter temperature − 15° C., what allowance must be made for expansion in one of the 1,700 ft. spans of the Forth Bridge? (Bridge is made of steel the coefficient of linear expansion of which = 0·000012.)

(7) The length of the tubular railway bridge across the Menai Straits is 461 metres. Find the total expansion of this iron tube between − 5° C. and + 35° C.

(8) A block of copper occupies a volume of a cubic foot at 100° C. What volume will it occupy at 0° C.?

(9) Describe how you would measure the coefficient of expansion of such a substance as a diamond.

(10) Explain why it is a sufficiently near approximation in general to take the coefficient of volume expansion as three times the coefficient of linear expansion. Calculate the error p.c. involved in this approximation in the case of calculating the cubical expansion through 100° C. of a body whose coefficient of linear expansion is 0·00001234.

(11) Describe and explain the method of measuring linear expansion of solids by means of interference bands.

PRACTICAL.

(2) Measure coefficient of expansion of a metal bar.

CHAPTER IV

EXPANSION OF LIQUIDS

Density.—The mass of unit volume of a substance is termed the density of that substance.

Using the cubic centimetre and the gram as the respective units of volume and mass, the density of a substance will be equal to the mass (in grams) of 1 c.c. of the substance.

Let us suppose that at a particular temperature m grams of a substance occupy a volume of v cubic centimetres. Then, to obtain the density, ρ, of the substance, we may proceed as follows.

v c.cs. possess a mass of m grams.

$\therefore$ 1 c.c. will possess a mass of $\frac{m}{v}$ grams.

$$\therefore \rho = \frac{m}{v}.$$

If the mass m of a certain quantity of a substance is known as well as the density ρ, then the volume occupied by the m grams may be determined from the equation

$$v = \frac{m}{\rho}.$$

If the volume v and the density ρ are known, and the mass m is required, we have

$$m = v\rho.$$

In most cases the density of a substance will vary with the temperature. This is obvious when we remember that 1 gram of the substance will generally occupy different volumes at different temperatures.

Expansion of Hollow Vessels.—It may be well at the outset to examine into the connection between the increase in the volume enclosed by a vessel when it is subjected to a rise of temperature, and the coefficient of linear expansion of the substance of which the vessel is composed. We will consider the cases of cylindrical and spherical vessels.

1. *Cylindrical vessel.*—Let A B C represent the section of a thin-walled cylindrical tube, of radius r, and length l, at some stated temperature, for instance, at 0° C.

Then the length of the periphery of the tube at 0° C. $= 2\pi r$; length of the periphery of the tube at t° C. $= 2\pi r\,(1 + at)$ if $a =$ the coefficient of linear expansion of the substance of which the tube is composed.

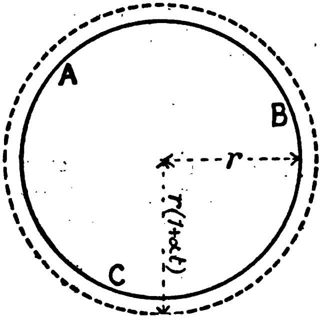

FIG. 32.—Expansion of a hollow vessel.

$\therefore$ Radius of tube at t° C. $= r(1 + at)$.
Sectional area of tube at t° C. $= \pi\{r(1 + at)\}^2$.
The length of the tube at t° C. $= l(1 + at)$.

$\therefore$ Volume enclosed by tube at t° C.

$$= \begin{matrix}\text{sectional area} \times \\ \text{length, both at } t^\circ\end{matrix} \left\{\begin{aligned} &= \pi\{r(1 + at)\}^2 l(1 + at). \\ &= \pi r^2 l(1 + at)^3. \\ &= \pi r^2 l(1 + 3at\ .\ .\ ). \quad (\textit{See}\ \text{p. } 59.)\end{aligned}\right.$$

But $\pi r^2 l =$ vol. enclosed by tube at 0° C., and $3a =$ the coefficient of cubical expansion of the glass.

Hence the increase in the volume of a hollow tube, resulting from a given rise of temperature, is the same as would be produced under similar conditions in a solid body occupying the same initial volume as that enclosed by the tube, and composed of the same substance as its walls.

2. The alteration in the volume of a spherical shell may be treated similarly. Let A B C now represent a section passing through the centre of the sphere.

Length of circumference of circular section at 0° C. $= 2\pi r$.

" " " " " t° C. $= 2\pi r(1 + at)$.

∴ Radius of circular section at t° C.

$$= \text{radius of sphere at } t^\circ \text{ C.} = r(1 + at).$$

Volume enclosed by sphere at 0° C. $= V = \frac{4}{3}\pi r^3$.

" " " " t° C. $= \frac{4}{3}\pi r^3(1 + at)^3$.

$$= V(1 + 3at + \ldots).$$

∴ Increase in volume of sphere due to heating through t° C.

$$= V \times 3at = V \times \text{coeff. of cub. exp.} \times t.$$

The student may be left to apply similar reasoning to the case of a cube, when it will be seen that the conclusion derived above for the case of a cylindrical tube may be generalised for the case of the volume enclosed by a vessel of any form.

Experiments made on the lines laid down in the last chapter, in order to determine the coefficient of linear expansion of glass, give no very trustworthy information which can be applied to vessels blown from glass tubing. During the melting and blowing the coefficient of expansion of glass is often somewhat altered, whilst different samples of glass vary very much one from another. Consequently, it becomes necessary to determine the coefficient of cubical expansion of a glass vessel after that vessel has been made.

Determination of the coefficient of Cubical Expansion of the Glass of which a Bulb is composed.—The coefficient of absolute expansion of mercury has been obtained by Regnault, using a method subsequently to be explained, in which no correction is necessary for the expansion of the containing vessel. By the aid of Regnault's results the absolute expansion of a vessel can be determined, and subsequently the absolute expansion of any liquid may be found.

The method to be employed is as follows:—

EXPT. 15.—A bottle, of the shape shown in Fig. 33, is blown from a piece of glass tubing. The best size for the bottle will depend on the balance which is to be used in weighing it when full of mercury. It is best not to use a sensitive chemical balance for this purpose, as doing so will necessitate the bottle being made very small. A spherical bulb, 1½ inches in diameter, will hold nearly 400 grams of mercury. A constriction is made in the neck of the bottle, and a file mark made at this point will serve to indicate the position which the surface of the mercury or other liquid should occupy. The bottle may be provided with a flat bottom, as long as the glass is not made so thin that the pressure of the mercury is likely to deform it.

The bottle should be washed with nitric acid and then with distilled water, and carefully dried by gently heating it and sucking air out through a piece of glass tubing. It is then weighed, and pure mercury is poured into it by means of a small funnel made by drawing out a piece of glass tube. Small bubbles of air on the glass can be removed by tilting the bottle when not quite full. The bottle is then placed in a beaker, and water is poured into the latter up to about the level of the constriction ; mercury is added or abstracted, as the case may require, so that the level of the mercury surface just coincides with the scratch in the neck. The temperature of the water having been observed, the bottle and its contents are weighed.

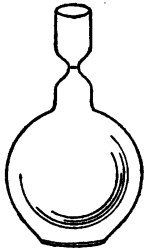

FIG. 33.—Dilatometer.

The bottle containing the mercury is then replaced in the beaker. The whole may now be heated on a sand bath up to about 90° C. When this temperature, observed by means of a thermometer dipping in the water, has been maintained constant for several minutes, mercury is carefully drawn out of the neck of the bottle by means of a small pipette, till the surface of the remainder just coincides with the scratch. The mercury which has been withdrawn is carefully run into a weighed watch-glass, and its mass is determined, a chemical balance being used for this purpose.

Let W = mass of mercury filling bottle at initial temperature.
w = mass of mercury removed at final temperature.
ρ = density of mercury at initial temperature.
t = difference between initial and final temperatures.

If the volume of the bottle had remained constant during the experiment, we might have reasoned as follows :—

A mass $(W - w)$ grs. of mercury which occupies a volume of

$\frac{W - w}{\rho}$ c.cs. at the initial temperature, is increased in volume by $\frac{w}{\rho}$ c.cs. when heated through $t°$ C.

∴ 1 c.c. of mercury, when heated through 1° C., is increased in volume by $\frac{w}{\rho} \cdot \frac{\rho}{W - w} \cdot \frac{1}{t} = \frac{w}{(W - w)t}$.

Since, however, the volume enclosed by the bottle is itself altered during the experiment, the quantity $\frac{w}{(W - w)t}$ represents, not the absolute coefficient of expansion of mercury, but the **coefficient of apparent expansion of mercury in glass.**

In order to take into account the expansion of the glass, we must proceed as follows :—

Let V = volume enclosed by bottle at initial temperature,
g = coefficient of cubical expansion of glass.

Then volume enclosed by bottle at final temperature = $V(1 + gt)$.
Increase in volume of bottle = Vgt.

Thus $(W - w)$ grs. of mercury, occupying a volume of $\frac{W - w}{\rho}$ c.cs. at initial temperature, are increased in volume by $\left\{\left(\frac{w}{\rho}\right) + Vgt \text{ c.cs.,}\right\}$ when heated through $t°$ C.

∴ 1 c.c. of mercury at the initial temperature will, when heated through 1° C., be increased in volume by

$$\left(\frac{w}{(W - w)t} + \frac{V}{\frac{W - w}{\rho}} g\right) \text{ c.cs.}$$

But $V = \frac{W}{\rho}$ and therefore $\frac{V}{\frac{W - w}{\rho}}$ may be taken as equal to 1. (It will not generally differ from unity by more than 1 or 2 per cent.)

Hence, if m = coefficient of absolute expansion of mercury.
m_g = coefficient of apparent expansion of mercury in glass.

$$m_g = \frac{w}{(W - w)t},$$

$$\text{and } m = \frac{w}{(W - w)t} + g = m_g + g.$$

i.e., **the coefficient of absolute expansion of mercury is approximately equal to the coefficient of apparent expansion of mercury in glass, increased by the coefficient of cubical expansion of glass.**

Therefore,[1] $g = m - m_g$.

According to Regnault, the mean value of m for temperature between 0° and 100° is ·00018153. . .

Hence this value, together with the value determined for the coefficient of apparent expansion of mercury in glass, will suffice to determine the coefficient of cubical expansion of glass.

To determine the coefficient of absolute expansion of water, &c.—

EXPT. 16.—The same bottle as that used for the last experiment is emptied, cleaned with nitric acid, and finally filled with water. It is then immersed in a beaker of water, which is boiled for some time, until all the air dissolved in the contained water has been expelled.

The temperature of the water in the beaker is then maintained constant at about 80° C. for the space of 8 or 10 minutes, when the water surface in the bottle is adjusted to be level with the scratch, and the bottle is removed from the beaker, dried, and weighed. The weighing may be performed on a sensitive chemical balance, but the bottle should first be allowed to cool, as the currents of air set in motion by the hot bottle will produce errors.

Similar operations may be performed at 70°, 60°, 30°, 20°, 10°, 0° C., the water in the beaker being cooled with ice shavings for the last experiments. Finally, the coefficients of expansion for these various values may be calculated, using the previously determined value of the coefficient of expansion of glass.

EXPT. 17.—The expansion of water can also be determined in another manner. A glass bulb about 2 in. in diameter is weighted with shot till it will just sink in cold water. The neck of the bottle is then drawn out and sealed, and the drawn out portion bent into a hook (Fig. 34). The bulb is suspended by means of a horsehair from the

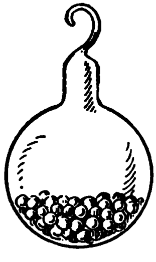

FIG. 34.—Weighted glass bulb, for determining expansion of a liquid.

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[1] For accurate work, we should use the exact equation, $g = (m - m_g)\frac{W - w}{W}$.

beam of a balance, and weighed. A small three-legged table is then placed above one of the balance pans, and a beaker of hot water is supported on this, so that the bulb is entirely immersed when the beam is swinging (Fig. 35).

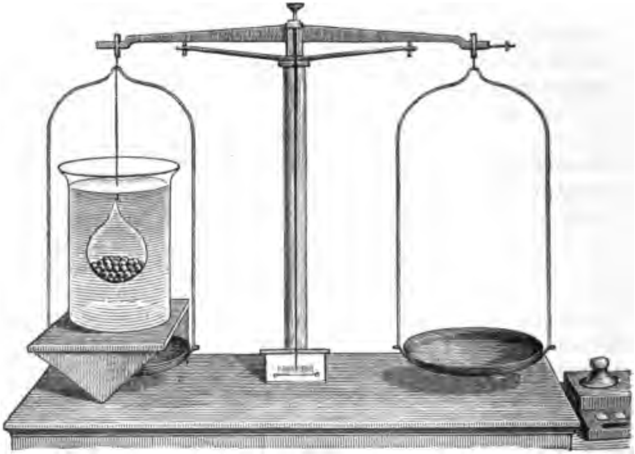


Fig. 35.—Arrangement for determining the expansion of a liquid by weighing a body of known expansibility in it.

Obtain the apparent masses of the bulb when suspended in water at two or three different temperatures, and deduce the mass of the water displaced in each instance.

Let W = true mass of bulb.
W_1 = apparent mass of bulb suspended in water at temp. t_1° C.
W_2 = ,, ,, ,, ,, t_2° C.
g = coefficient of cubical expansion of glass.
ρ = the (unknown) density of water at t_1° C.

Then, mass of water displaced at t_1° C. = $(W - W_1)$ grams.

$$\text{Volume of bulb at } t_1^\circ \text{ C.} = \frac{W - W_1}{\rho} \text{ c.cs.}$$

$$\therefore \text{ Volume of bulb at } t_2^\circ \text{ C.} = \frac{W - W_1}{\rho}\left\{ 1 + g(t_2 - t_1) \right\} \text{ c.cs.}$$

But mass of water displaced at t_2° C. = $(W - W_2)$ grams.

If this mass of water were cooled to t_1° C., it would occupy a volume of $\frac{W - W_2}{\rho}$ c.cs. But at t_2° C. it actually occupied a volume of

$$\frac{W - W_1}{\rho}\{1 + g(t_2 - t_1)\} \text{ c.cs.}$$

∴ Increase in volume of $\frac{W - W_2}{\rho}$ c.cs. of water, when heated through

$$(t_2 - t_1)^\circ \text{C.} = \frac{W - W_1}{\rho}\{1 + g(t_2 - t_1)\} - \frac{W - W_2}{\rho}$$

$$= \frac{W_2 - W_1}{\rho} + \frac{W - W_1}{\rho} g(t_2 - t_1).$$

∴ Increase in volume of 1 c.c. of water when heated through

$$1^\circ \text{C.} = \left\{\frac{W_2 - W_1}{\rho} + \frac{W - W_1}{\rho} g(t_2 - t_1)\right\} \div \frac{W - W_2}{\rho}(t_2 - t_1)$$

$$= \frac{W_2 - W_1}{(W - W_2)(t_2 - t_1)} + \frac{W - W_1}{W - W_2} g.$$

Further, the quantity by which g is multiplied will be very nearly equal to 1. Hence, finally, if β is the mean coefficient of absolute expansion, of water between t_1° and t_2° C.,

$$\beta = \frac{W_2 - W_1}{(W - W_2)(t_2 - t_1)} + g.$$

Experiments to determine the behaviour of water with regard to expansion, between the temperature 0—10°, will be described later on in this chapter.

Coefficient of Absolute Expansion of Mercury.—Before giving an account of Regnault's experimental determination of the absolute expansion of mercury, a simple modification of the apparatus previously used by Dulong and Petit for the same purpose will be described. This apparatus can be made, with the exercise of a little care, by any one possessing a slight amount of skill in bending glass tubing, and will permit of tolerably accurate results being obtained.

The immediate object of this experiment is to determine the ratio of the densities of mercury at two different temperatures. Having obtained this, a simple calculation will suffice to determine the coefficient of expansion.

Now the ratio of the densities of two liquids, such for instance as mercury and water, may be obtained by pouring mercury into a U-tube, and then introducing a column of water into one of the limbs above the mercury. If we imagine a horizontal plane to be drawn through the surface of separation of the water and mercury, this plane will cut off a short column of mercury in the other limb of the tube, the height of this column being such that the pressure due to it is just equal to the pressure produced by the water column. It must be remembered that *pressure* denotes *force per square cm.*; hence the pressure produced by a column of water H_1 cm. high is obviously equal to the force exerted by gravity on a column of water of 1 sq. cm. sectional area, and H_1 cms. long. This force is equal to $g \times 1 \times H_1 = gH_1$ dynes where g is the acceleration due to gravity. Similarly, if ρ is the density of mercury the pressure due to a column of mercury H_2 cms. high will be equal to $g\rho H_2$.

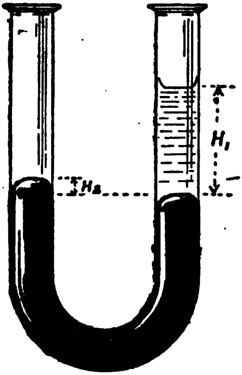


FIG. 36.—U-tube containing mercury and a less dense liquid.

The condition that these pressures should be equal, gives

$$g\rho H_2 = gH_1 \text{ or } \rho H_2 = H_1.$$

Hence the condition that two liquid columns should produce equal pressures, is obtained by equating the heights of the columns multiplied by their respective densities.

It will be noticed that no error is introduced into this result by irregularities in the sectional areas of the limbs, or even if any variations in the dimensions of the limbs occur during the course of the experiment.

The application of this principle to the determination of the absolute expansion of mercury may best be explained when the construction of the necessary apparatus has been described.

Fig. 37 shows front and side views of the apparatus. It may be constructed as follows :—

EXPT. 18.—A wooden stand, consisting of a base 6″ × 9″, and an upright board 24″ × 9″, is made from ½-inch pine. Four blocks, about 1″ × 2″ × ¾″, are provided, and are ultimately fixed in the positions

A_1 A_2 A_3 A_4 (Fig. 37). These blocks are slightly grooved on their front surfaces, so as to admit of the pieces of 1″ glass tubing T_1, T_2 being fastened to them at a distance of 7″ from centre to centre. Each of the glass tubes T_1, T_2, is 18″ long, and is provided at both ends with sound corks. Each cork is bored centrally to take a glass tube of about ¼″ internal diameter, and excentrically to take another tube of rather smaller size.

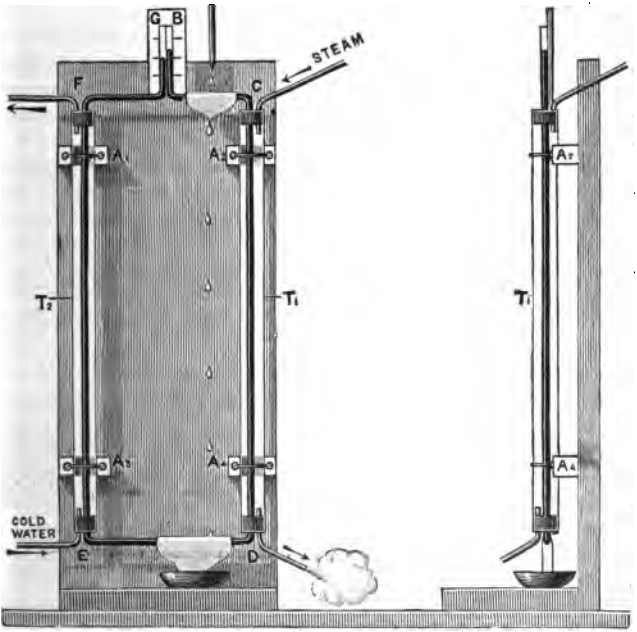


Fig. 37.—Apparatus for Determining the Absolute Expansion of Mercury.

The most important part of the apparatus is the continuous glass tube BCDEFG. A piece of ¼″ glass tubing 5 feet long is taken and cleaned by drawing through it a small plug of wet cotton wool attached to the end of a string. The tube is dried by gently heating and drawing air through it, and then twice bent at right angles at D and E, two points 7″ apart and equidistant from the middle of the piece of tubing. Care should be taken that it is in both cases bent accurately at right angles, and that the bent pieces lie in one plane. The ends of these tubes are pushed through the central holes in the corks fitted to the tubes T_1 and T_2, when the whole may be laid on a flat table with the projecting ends of the glass tube over the edge.

The next operation is to make the rectangular bends at C and F. This may best be done by the aid of a small luminous gas flame. The bends should be made as near to the corks as possible. At this stage it will be impossible to bend both tubes so as to lie in the same plane as the rectangle CDEF, but they may be bent so as to lie one on the other, and a final adjustment made subsequently.

Both tubes must then be bent so that a few inches near their extremities lie parallel and side by side (see Fig. 37). The blocks A_1, A_2, A_3, A_4, having been placed in position, the whole arrangement may be fixed by means of copper wires encircling T_1 and T_2, and wound round the heads of nails projecting from the blocks.

Bent tubes are fitted to the excentric holes in the corks, as shown in the figure.

A small millimetre scale, preferably engraved on a piece of looking-glass, is fixed behind the upright tubes ending at B and G.

Clean mercury is then poured into the tube BCDEFG. When a small amount has been poured in, this must be run backwards and forwards so as to remove any air bubbles on the sides of the tube. This operation must be repeated at intervals whilst the tubes are being filled to within about two inches from their ends.

The tubes T_1 and T_2 are then set upright, with the tube DE horizontal. The mercury surfaces should give equal readings on the scale; if they do not, the disagreement may be due to the tubes B and G being of different diameters, thus giving rise to capillary forces which differ in the two cases. Any disagreement must be noted, and applied as a correction to all subsequent readings.

Steam is afterwards led through the right-hand tube T_1, whilst a stream of water at the temperature of the air is led through T_2. The temperature of the water on entering and leaving T_2 must be noted. Pieces of blotting paper are placed on the horizontal tubes near to C and D, and water which has stood some time in the air is allowed to drip on these from a burette. This is to prevent heat from travelling along the mercury column from the part enclosed in the tube T_1.

It will be found that the mercury stands at a higher level in the tube B than in G. The explanation of this is simple. The mercury surrounded by the steam jacket having been heated, has expanded, and its density has consequently become smaller. Hence, in order to balance the cold mercury column on the left-hand side of the apparatus, a greater total length of column is required on the right-hand side.

It will, for simplicity, be assumed that the tubes DE, and those proceeding from C and F, are horizontal, and therefore that length CD = length FE = H (say); also that the temperature of the water passing through T_2 is equal to that of the air.

If the vertical column of mercury in B is h_1 cms. long, that in the neighbouring tube G being h_2 cms. in length, and if ρ_t = density of mercury at the temperature of the air, ρ_{100} = density of mercury at 100° C., we have

$$\text{Pressure at D} = h_1\rho_t + H\rho_{100}$$
$$,, \quad \text{E} = h_2\rho_t + H\rho_t.$$

Since D and E are in the same horizontal plane, the pressures at these points must be equal.

$$\therefore\ h_1\rho_t + H\rho_{100} = h_2\rho_t + H\rho_t$$
$$H\rho_{100} = \rho_t\{H - (h_1 - h_2)\}$$
$$\therefore\ \frac{H}{\rho_t} = \frac{H - (h_1 - h_2)}{\rho_{100}} \quad . \quad . \quad . \quad (1)$$

But ρ_{100} = mass, in grs., of 1 c.c. mercury, at a temperature of 100° C.

$\therefore$ 1 grm. of mercury, at 100° C., occupies a volume of $\frac{1}{\rho_{100}}$ c.cs.

Similarly ρ_t = mass in grms. of 1 c.c. of mercury at $t°$ C..

$\therefore$ 1 grm. of mercury at $t°$ occupies a volume of $\frac{1}{\rho_t}$ c.cs.

Further, volume of 1 grm. of mercury at 100° = $\{1 + m(100 - t)\}$ × volume of 1 grm. of mercury at $t°$ C.,

if m = mean coefficient of expansion of mercury between 100° and $t°$ C.

$$\therefore\ \frac{1}{\rho_{100}} = \frac{1 + m(100 - t)}{\rho_t}.$$

Substituting this value in (1) we get

$$\frac{H}{\rho_t} = \left\{\frac{1 + m(100 - t)}{\rho_t}\right\}(H - h_1 + h_2).$$

$$\therefore\ H = \{1 + m(100 - t)\}(H - h_1 + h_2).$$

Re-arranging, we get

$$m(100 - t)(H - h_1 + h_2) = H - H + h_1 - h_2 = h_1 - h_2,$$

$$\therefore\ m = \frac{h_1 - h_2}{(100 - t)(H - h_1 + h_2)}.$$

If $h_2 - h_1$ is small in comparison with H, we shall have

Mean coefficient of absolute expansion of mercury $= m = \dfrac{h_1 - h_2}{(100 - t)H}$.

It will be noticed that $h_1 - h_2$ is equal to the difference in level of the two free mercury surfaces.

It may be remarked that the results of this experiment are not quite unaffected by the expansion of the glass tubes. Thus if the length CD = length FE at t° C., then CD will be increased in length when heated. Error from this cause may be avoided by measuring the lengths CD and FE whilst at their final temperatures. The error incurred is, however, in any circumstances smaller than that arising when experiments on the expansion of liquids in bulbs, &c., are in question. In fact, in the present experiment the coefficient of linear expansion of glass occurs, possessing only one-third of the value of the coefficient of cubical expansion, the correction to be applied in other cases. It may be left as an exercise to the student to show that

$$m = a + \frac{h_1 - h_2}{(100 - t)\,H}$$

where a is the coefficient linear expansion of the glass.

Regnault's Determination of the Coefficient of Absolute Expansion of Mercury.—Regnault used an arrangement essentially similar to that just described to perform a long series of experiments; but the apparatus most closely associated with his name was constructed on a slightly different plan. The general principle of this apparatus may be understood from Fig. 38. Two upright tubes, AA′, BB′, are connected together, at the top by a straight horizontal tube of fine bore AB, and at the bottom bv a tube A′CEFDB′ bent into an inverted U near its centre. The upper tube has a small hole bored in its upper surface at K; and a connecting tube, leading to a receptacle containing compressed air, is attached to the top of the inverted U at G. Mercury is poured into the arrangement at A or B, and a sufficient pressure produced in the air chamber to depress the surfaces of the mercury in CE and DF to about the middle of these tubes. If the mercury in AA′ is at the same temperature as that in BB′, the surfaces of the mercury in the central tubes will, of course, be in the same horizontal plane.

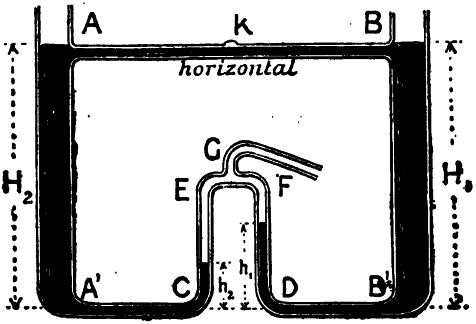


Fig. 38.—Diagrammatic Representation of Regnault's Apparatus.

If, now, the mercury in one of the side tubes, say AA′, is raised to a temperature above that of the other BB′, the mercury will stand higher in DF than in CE.

Let h_1 = height of mercury surface in DF above the centre of the tube B′D, and h_2 = height of mercury surface in CE above centre of the tube A′C.

Let H_1, H_2, be the distance from the free mercury surfaces at B and A to the centre of the tubes DB′ and A′C respectively.

Let t_1 = temp. of mercury in BB′ and the tubes CE and DF and ρ_1 its density; also t_2 = temp. of mercury in AA′, and ρ_2 its density.

Let P = the excess of the pressure in the air chamber, above the atmospheric pressure.

Then, since the pressures at the ends of the tube DB′ must be equal, we have

$$P + h_1\rho_1 = H_1\rho_1 \therefore P = H_1\rho_1 - h_1\rho_1.$$

Similarly with regard to the pressures at the ends of A′C

$$P + h_2\rho_1 = H_2\rho_2 \quad \therefore \quad P = H_2\rho_2 - h_2\rho_1.$$

Combining these equations we have

$$H_1\rho_1 - h_1\rho_1 = H_2\rho_2 - h_2\rho_1.$$

$$\therefore \ \rho_1(H_1 - h_1 + h_2) = H_2\rho_2.$$

$$\therefore \ \frac{H_1 - h_1 + h_2}{\rho_2} = \frac{H_2}{\rho_1}.$$

By reasoning precisely similar to that employed on p. 75, it may be shown that

$$\frac{1}{\rho_2} = \frac{1 + m(t_2 - t_1)}{\rho_1}.$$

Hence

$$\frac{(H_1 - h_1 + h_2)\{1 + m(t_2 - t_1)\}}{\rho_1} = \frac{H_2}{\rho_1}.$$

$$(H_1 - h_1 + h_2)\{1 + m(t_2 - t_1)\} = H_2.$$

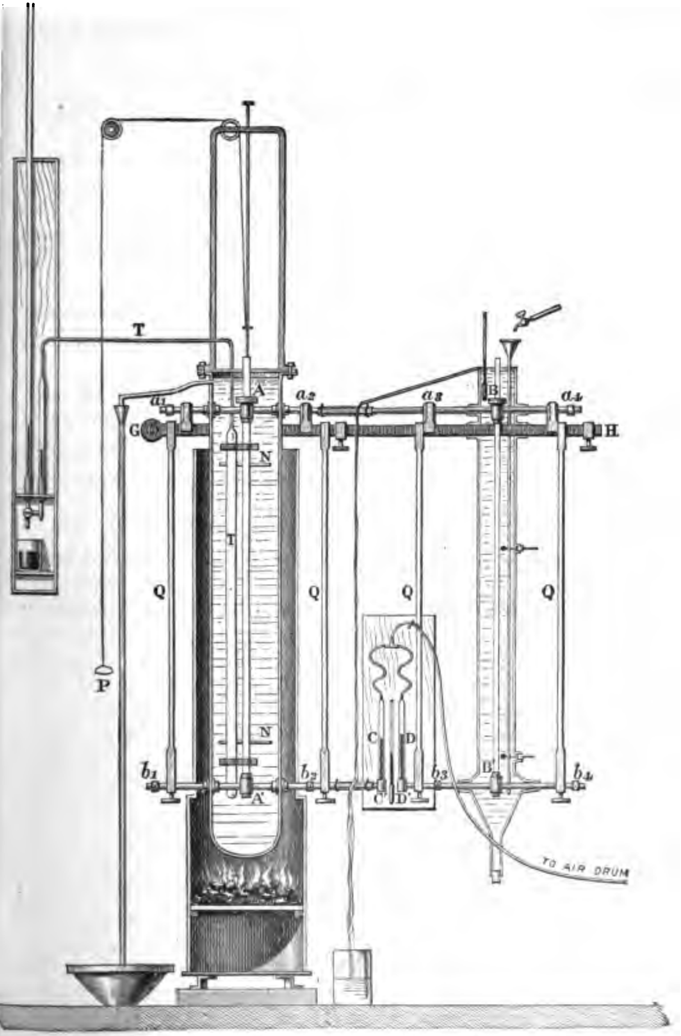
Hence, following a similar method to that employed on p. 76, we get

$$m = \frac{H_2 - H_1 + h_1 - h_2}{(H_1 - h_1 + h_2)(t_2 - t_1)}.$$

It should be noticed that the use of the compressed air forced into the upper part of the tubes CE and DF might have been avoided by making these tubes sufficiently long. In that case, however, it would have been difficult to arrange that the temperature of the mercury throughout the whole lengths of these columns should have been uniform.

Fig. 39 represents the actual apparatus used by Regnault. GH represents an iron bar, supporting the tube AB in a horizontal position. The tube AA′ was surrounded by a jacket filled with oil, which could be heated by a fire beneath it. The other upright tube BB′ was surrounded by a jacket through which cold water circulated, whilst a stream of cold water prevented heat from travelling along the mercury in the horizontal tubes. The temperature of the oil surrounding AA′ was obtained by means of an air thermometer, the bulb T of which extended the whole length of AA′. The use of the other parts of the apparatus may easily be seen by comparison with the diagrammatic sketch (Fig. 38).

In performing an experiment, the pressure in the air chamber



IG. 39.—Regnault's Apparatus for Determining the Absolute Expansion of Mercury. (P)

was increased until mercury just began to flow from the central hole in the horizontal tube AB. The lengths of the vertical mercury columns were measured from this level.

Regnault's object was not alone to determine the coefficient of expansion of mercury at a single temperature, but also to find how the expansion varied with the initial temperature of the mercury. If 1 c.c. of mercury is increased in volume by a certain amount when heated from 0° to 1° C., it does not follow that 1 c.c. of mercury at 100° C. will expand by the same amount when heated to 101° C. The result obtained will to an extent vary with the thermometric scale chosen.

Variations in value of *m* with Thermometric System adopted.—With a mercurial scale, temperature is defined according to the following conditions:—

Let us suppose 1 c.c. of mercury, at the temperature of melting ice, to be increased to 1 + A c.cs. at the temperature of steam under standard conditions. Then each degree Centigrade will correspond to an increase in volume of $\frac{A}{100}$ c.cs. Thus at $t_1°$, the volume occupied by the mercury in question will be $1+\frac{A}{100}t_1$, at $t_2°$, it will be equal to $1+\frac{A}{100}t_2$. Thus we have, $(1+\frac{A}{100}t_1)$ c.cs. of mercury at $t_1°$, increases in volume to

$$(1+\frac{A}{100}t_2)\text{ c.cs. at } t_2°.$$

∴ 1 c.c. of mercury at $t_1°$ is increased in volume by $\dfrac{\frac{A(t_2-t_1)}{100}}{1+\frac{A}{100}t_1}$ when heated to $t_2°$.

∴ Coefficient of expansion of mercury at $t_1°$

$$=\frac{\frac{A(t_2-t_1)}{100}}{1+\frac{A}{100}t_1}\div(t_2-t_1)=\frac{\frac{A}{100}}{1+\frac{A}{100}t_1}.$$

Therefore if temperatures are measured by means of a mercury thermometer, the coefficient of expansion of mercury will decrease as the initial temperature $t°$ C. of the mercury is increased. For reasons which have been in part explained (Ch. II.) and will be amplified when we come to consider the thermometric properties of gases, an air (or, better still, a hydrogen) thermometer always forms the ultimate standard in measuring temperature. This at 100° and at 0° C. will agree with the mercury thermometer; but other temperatures as indicated by the air and mercury thermometers will not agree exactly.

With the air thermometer, temperatures may be measured as follows :—Let a certain quantity of air at the temperature of melting ice occupy a certain volume under a pressure P, and let it be necessary to increase this pressure by p in order to maintain this air at the same volume at the temperature of water boiling under standard conditions. Then an intermediate temperature t° C. will correspond to a pressure of $P + \frac{p}{100}t$, the air being maintained throughout at its initial volume.

Regnault found that when temperatures are measured by an air thermometer, m was very nearly constant for temperatures between 0° and 100° C. For very high temperatures its value differed somewhat considerably from its value at low temperatures.

Between 0° and 100° C. the mean value for the coefficient of cubical expansion of mercury is ·00018153.

Coefficients of Expansion of Liquids.—Two methods of determining the coefficient of expansion of a liquid have already been described. An improved form of apparatus for determining the same quantity will here be mentioned.

Fig. 40 represents a **Pyknometer.** This consists of a wide tube AB joined at both ends to thermometer tubes of fine bore, which are bent as shown, the parts CD, EF being in a straight line. To fill this arrangement, the end C of the tube DC (which is here drawn out so as to possess a very fine orifice) is placed below the surface of the liquid, AB meanwhile being inclined with B uppermost. A piece of indiarubber tubing having been placed over the end F, liquid is sucked into the apparatus till the whole is filled.

The pyknometer is then placed in a beaker of water, and is supported by resting the tubes CD, EF on the rim of the beaker. After having been left for a sufficient time for the contained liquid to have attained the temperature of the surrounding water, the pointed end E of the capillary tube is touched with a piece of blotting paper, and liquid withdrawn in this manner till the meniscus in the tube EF is seen to just coincide with the scratch G.

The pyknometer and its contents are then weighed and the above operations repeated, only with the water contained in the beaker kept at a higher temperature. The necessary calculations are similar to those already explained. (pp. 67-68.)

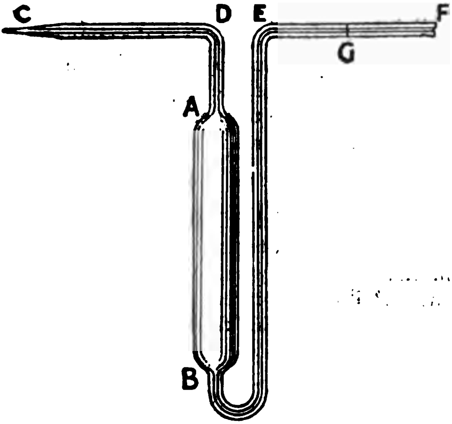


Fig. 40.—A Pyknometer.

To determine the Expansion of Water between 0° and 10° C.

Expt. 19.—A simple form of apparatus for this experiment may be made as follows[1]:—

A water thermometer, of the shape shown in Fig. 41, is made out of glass. The bulb is cylindrical, so as to present a large cooling surface, and should contain from two to three hundred cubic centimetres of water. The relative sizes of the bulb and tube must be selected after the performance of a calculation similar to that given on p. 6; the expansion of water for temperatures between 0° and 10° can be derived from the table on p. 469.

[1] *See a description by Mr. H. E. Hadley in "The School World,"* June, 1901.

In order to obtain the best results, about one-seventh part of the volume of the bulb should be filled with mercury, M, the rest of the space being filled with water, W. By this means the expansion of the bulb is corrected for. The total increase in volume of the bulb when heated is equal to the increase in volume of the mercury, so that the volume occupied by the water remains unchanged. (See Question 3, p. 88.)

The bulb must be filled with distilled water which has been well boiled, in the manner explained, with regard to a mercury thermometer on p. 8. It is best not to seal up the tube of the water thermometer; a short column, O, of heavy paraffin oil can be used to prevent contact between the water and the atmosphere.

To perform an experiment, the bulb is immersed in water contained in a suitable vessel, and a steel scale, or better still, a scale engraved on a piece of looking glass, is fastened behind the tube with soft red wax. Finally a thermometer is hung in the water in order to indicate the temperature.

The best means by which the water may be cooled is by adding ice shavings, cut with a broad chisel from a large block of ice. Stir the water well, and try to maintain the temperature indicated by the thermometer constant for several minutes before each reading. The observations to be taken are, the positions of the water surface (reading from the *lowest* edge of its curved surface), and the corresponding temperatures of the surrounding water. When you have cooled the water down to nearly 0° C., taking readings (say) at 15°, 12°, 9°, 7°, 6°, 5°, 4°, 3°, 2° and 1°, allow the water to rise in temperature, stirring well all the while, and take similar observations in a reverse order.

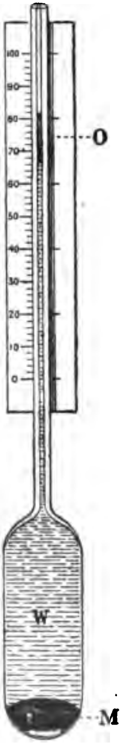


Fig. 41. Apparatus for determining the temperature of maximum density of water. W, water; M, mercury; O, short column of oil.

Take the mean of the two readings of the position of the water surface at any temperature (when cooling and when heating) to represent the true reading for the given temperature. Plot a curve similar to Fig. 42, temperatures being marked off horizontally, and the readings for the height of the water surface vertically.

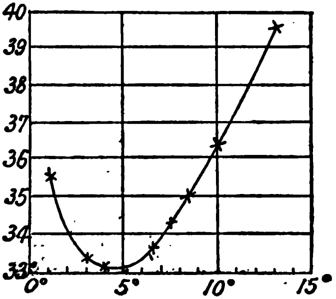


FIG. 42.—Curve, showing the expansion of water between 0° and 10° C.

The curve shows very plainly that the surface of the water in the narrow tube falls as the water is cooled, till a temperature of about 4° C. is reached; after that the surface rises till 0° C. is reached.

Consequently water is denser (or 1 c.c. of water has a greater mass) at 4° C. than at any other temperature. Further notice that the curve is very nearly flat in the neighbourhood of 4° C., so that a small variation in the temperature will make little difference in the density of water.

(The curve given shows that while the temperature was changing from 6·8° C. to 4° C., giving a fall of temperature of 2·8° the water surface fell ·4 cm.; whilst for a change of temperature from 10° C. to 7·5° C., *i.e.* a fall of 2·5°, the water surface fell 2 cm.)

For this reason the **unit of mass in the metric system has been defined as the mass of 1 cc. of water at a temperature of 4° C. This unit of mass is called a gram.**

EXPT. 20—The value of the expansion of water between 0° and 10° C. may also be obtained by the use of the method explained in experiment 17, p. 69, cooling the water by adding ice shavings.

This method was used by Matthiessen; the coefficient of expansion of the bulb was first determined by finding the mass of mercury which it contained at various temperatures.

Hälström used a piece of glass rod instead of the bulb, and determined the coefficient of linear expansion of the rod by Ramsden's method (see p. 46).

Maximum Density of Water.—Fig. 43 represents Hope's well-known apparatus for determining the temperature at which water possesses a maximum density. A cylindrical glass vessel is surrounded, at about half its height, by an annular trough, which may be filled with a mixture of broken ice and salt, thus forming a freezing mixture. Two thermometers indicate the respective temperatures of the water at the top and bottom of the cylindrical vessel.

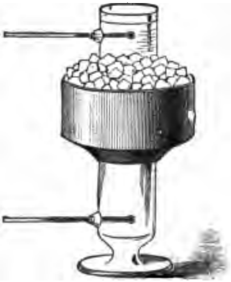


FIG. 43—Hope's Apparatus for determining the temperature corresponding to the maximum density of water.

As long as the density of the water is increased by cooling, the colder water will sink, thus causing the temperature indicated by the lower thermometer to fall. This will go on until the lower thermometer indicates 4° C., the upper thermometer meanwhile remaining at its initial temperature. Soon after the lower thermometer has reached 4° C., the temperature indicated by the upper one will commence to fall, and will continue to do so till 0° C. is reached, and ice begins to form on the upper surface. The temperature indicated by the lower thermometer remains during this interval at 4° C.

Expansion of Liquids above their Boiling Temperatures and below their Solidifying Temperatures.—Pure liquids, particularly pure water, may be cooled considerably below their solidifying temperatures without becoming solid, as long as the containing vessel is quite clean, and dust and mechanical vibrations are avoided. Hence, if such a liquid is enclosed in a bulb provided with a tube like an ordinary thermometer, it is possible to study its behaviour at temperatures far below its solidifying point.

Despretz has thus studied the behaviour of water as far as a temperature of $-20°$ C. He found that water continued to expand as the temperature fell, until solidification occurred.

After solidification had occurred, however, the ice contracted with further cooling; **indeed, after water is frozen, any subsequent fall of temperature is accompanied by a contraction.**

When liquids are subjected to pressure, their boiling points are raised. We have already seen how this property has been utilised in the construction of high temperature thermometers. In an exactly similar manner we can study the expansion of a liquid at temperatures above its boiling point, by enclosing the liquid in a thermometer-shaped vessel, the space above its surface being occupied by some inert gas.

In this way it has been found that the coefficient of cubical expansion of a liquid increases as the temperature is raised, and may even, for high temperatures, be greater than that of the permanent gases. Thus Thirlorier found that the volume of liquid carbonic acid at 30° C. was one-and-a-half times the volume of the same liquid at 0° C., thus showing an expansion equal to four times that of air.

The expansion of a liquid which is raised to such a high temperature that it would boil if the pressure to which it is subjected were relaxed, has been found to be independent of the exact value of that pressure. Water, however, appears to form an exception to this rule. Thus the temperature of maximum density of water is lowered by about 1° C. when subjected to a pressure of 50 atmospheres.

Cubical Expansion of a Solid.—If a solid body be enclosed in a glass vessel of which the coefficient of expansion has been determined by the method already described (p. 66), and if some liquid such as mercury, of which the absolute expansion is known, be introduced so as to fill the space not occupied by the solid, the expansion of the latter may be easily determined by finding the apparent expansion of the mercury.

Fig. 44 shows a weight thermometer or dilatometer, arranged for this purpose. The narrow neck is drawn out after the solid bar has been introduced. The bar is provided with small projections to keep it from lying on the side of the dilatometer.

The instrument is filled by placing the end of the drawn out tube below the surface of some clean mercury, and driving out some of the contained air by heating; mercury subsequently enters as the dilatometer is allowed to cool. This process is repeated till all the air is expelled, when the mercury is boiled for a short interval in order to remove the gases condensed on the inside surface of the glass.

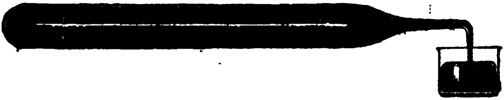


FIG. 44.—Weight thermometer, arranged to determine the cubical expansion of a solid. (P)

The apparent expansion of the mercury in this instrument is obtained in a manner exactly similar to that already explained (p. 68).

It may be remarked that the weight thermometer shown in Fig. 44 is often used for the determination of expansions, instead of that described on p. 67. Some care is, however, required in the filling it, whilst it possesses no marked advantages.

SUMMARY.

Density is defined as the mass of unit volume of a substance.

Thermal Expansion of a Hollow Vessel.—When a hollow vessel is heated. the increase in the enclosed volume is equal to that which a solid body, made of the same material as the walls of the vessel, and possessing a volume equal to that initially enclosed, would experience in similar circumstances.

The Coefficient of Apparent Expansion of a liquid is equal to the coefficient of absolute expansion of the liquid diminished by the coefficient of cubical expansion of the substance of which the enclosing vessel is composed.

The Coefficient of Absolute Expansion of Mercury was determined by Regnault by balancing a column of hot mercury against a column of cold mercury.

The Coefficient of Apparent Expansion of a liquid may be determined—

(1) By weighing a vessel filled with the liquid at two different temperatures.

(2) By weighing a body in air, and then when immersed in the given liquid at two different temperatures.

(3) By observing the height to which a liquid rises in the tube of a thermometer-shaped vessel when the whole is heated.

From these observations the coefficient of absolute expansion of the liquid can be determined if the coefficient of cubical expansion of the substance of which the vessel is composed is known.

The Temperature of Maximum Density of Water is 4° C.

The Coefficient of Cubical Expansion of a Solid Rod can be determined by enclosing it in a weight thermometer (or dilatometer) filled with mercury, and determining the apparent expansion of the latter substance.

When **ice is cooled below 0° C.** it contracts, and expands again on heating until melting commences.

When **water is cooled below 0° C.**, under such conditions that solidification does not occur, it expands as lower temperatures are reached.

QUESTIONS ON CHAPTER IV.

(1) Describe a method of determining the absolute expansion of mercury.

(2) Explain how to make a weight thermometer. If the coefficient of relative expansion of mercury in glass be $\frac{1}{6500}$, what mass of mercury will overflow from a weight thermometer which contains 400 grams of mercury at 0° C. when its temperature is raised to 100° C.

(3) If the coefficients of cubical expansion of glass and mercury are 0·000025 and 0·00018 respectively, what fraction of the whole volume of a glass vessel should be filled with mercury in order that the volume of the empty part should remain constant when the glass and mercury are heated to the same temperature?

(4) How may the absolute expansion of any non-volatile liquid be directly determined? Explain why the balancing of a hot against a cold column eliminates the expansion of the vessel. If the cold column at 4° C. were 60 cms. high, and the hot column at 95° C. were $\frac{1}{3}$ cm. higher, what would be the absolute coefficient of cubical expansion of the liquid?

(5) Describe the process of determining the coefficient of expansion of a liquid, like alcohol or paraffin, remembering the necessary preliminary determination of the expansibility of the glass vessel employed.

(6) How can the absolute expansion (*a*) of mercury, (*b*) of any other liquid, be determined?

(7) Describe an experiment which proves that the density of water is greatest at about 4° Centigrade.

(8) Describe a method by which you could find accurately the cubical expansion of a liquid relative to glass.

(9) How may the absolute expansion of mercury be determined?

(10) Show how far the statement, that the coefficient of apparent expansion of a liquid in glass is equal to the difference between the absolute expansibilities of glass and liquid, is a precisely accurate one; and describe a method of measuring the apparent expansibility of a liquid in glass.

(11) A long glass tube, with uniform capillary bore, has in it a thread of mercury which at 0° is 1 metre long. At 100° the thread is 16·5 mm. longer. If the average coefficient of volume expansion of mercury is 0·000182, what is the coefficient expansion of the glass?

(12) Find the reading of a mercury thermometer if the bulb and stem up to the zero graduation are exposed to a temperature of 300° C. while the remainder of the stem is at 20° C., assuming the coefficients of cubical expansion of mercury and glass to be 0·000180 and 0·000030 respectively.

PRACTICAL.

(1) Find the expansion of water between the temperature of the room and 80° C.

(2) Determine the expansion of water between two temperatures by weighing in it a solid of given expansion.

(3) Find the expansion of water between the temperature of the room and 50° C. given the expansion of glass.

(4) Blow a bulb on a glass tube of small bore, and measure the capacity of the same and that of each cm. length of the stem.

(5) Determine the coefficient of expansion of paraffin oil.

(6) Measure the coefficient of expansion of a liquid by a weighing method.

CHAPTER V

ELASTICITY AND THERMAL EXPANSION OF GASES

Relation between the Volume and the Pressure of a Gas.—The volume which a gas occupies depends, not only on its temperature, but also, and to an equal degree, on the pressure to which it is subjected. Hence before attempting to determine the laws governing the thermal expansion of gases, we must study the variation in volume of a gas when the pressure to which it is subjected is altered.

Fig. 45 represents an arrangement which may be used to study the relation between the volume and pressure of a gas.

AB is a hundred c.c. burette, furnished with a stopcock at A, and drawn out at B, so as to fit into a piece of indiarubber pressure tubing. A drying tube D, filled with large pieces of calcium chloride, is connected above the stopcock by means of a piece of ordinary indiarubber tubing.

The pressure tubing, joined at one end to B, is connected at its other end C with a glass tube, which in its turn fits tightly in a hole bored in an indiarubber stopper, closing the lower orifice of a mercury reservoir R. A bent side tube G is fused on to the tube just mentioned; the vertical portion of this side tube is placed in front of a centimetre scale, so that the height of the mercury in the reservoir may be accurately indicated.

The reservoir R is made from a wide-mouthed bottle of about 120 c.cs. capacity, in which a small hole has been drilled at H. Mercury can be introduced through this hole by means of a funnel with a bent tube.

The hole in the bottle may be bored by the help of a file which has been ground at one end to a three-cornered pyramidal point, and then hardened by being raised to a white heat and plunged

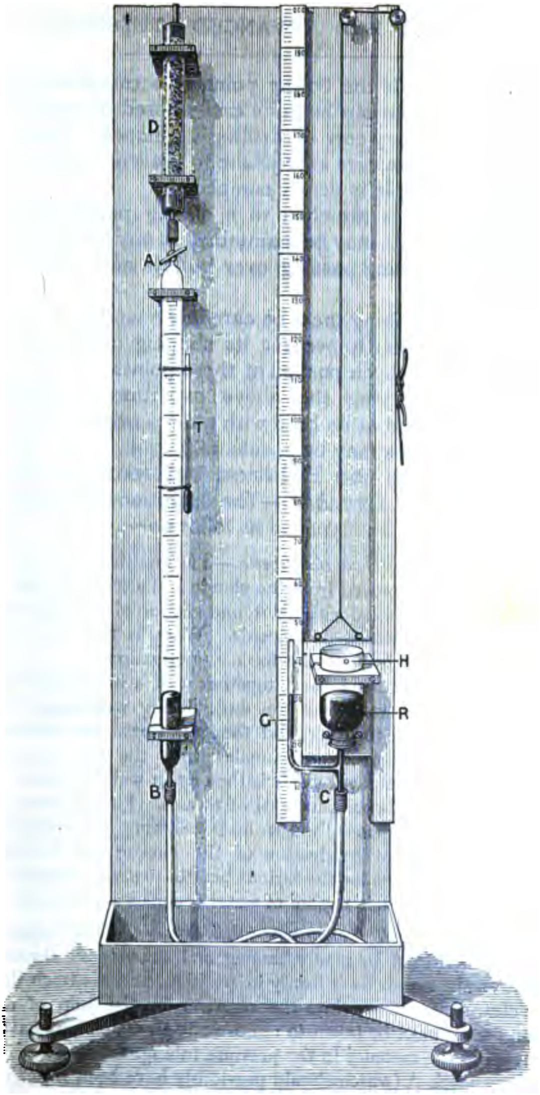


FIG. 45.—Apparatus for determining the relation between the pressure and volume of a gas, at constant temperature.

into cold water. If the boring point is occasionally dipped in turpentine, the hole can be quite easily bored by hand in a few minutes without any sort of drilling appliance. Indeed, if the latter is used, some care is requisite to prevent a fracture of the bottle when the hole is nearly completed.

The reservoir is attached to a sliding panel capable of a vertical motion. It may be maintained in any particular position by means of a string passing over pulleys near the top of the apparatus.

The pressure tubing must be carefully bound with copper wire at B and C, in order to prevent its slipping off the glass tubes over which it has been pushed at these points.

The stand carrying the above experimental arrangement should be provided at its base with a deep wooden tray to catch any mercury which may be accidentally spilt.

To determine the Relation between the Pressure and Volume of Dry Air.—The operations to be performed may conveniently be classified as follows :—

EXPT. 21.—*To calibrate the burette.*—The burette is detached from the tubes at its ends, removed from the stand, and after being cleaned with strong nitric acid, is filled with water, and supported in a vertical position with the closed stopcock downwards. Water is then run out till the meniscus just coincides with the 100 c.c. graduation.

Obtain a flat-bottomed flask, together with a watchglass which may be used to close the mouth of the flask during weighing. Weigh the watchglass and flask together, and then run water into the flask from the burette till the meniscus coincides with the 90 c.c. graduation. The flask and its contained water is then again weighed, and the above operation repeated for each interval of 10 c.cs. Finally, water is run off just down to the stopcock, so that after weighing, the volume between the stopcock and any graduation of the burette can be determined. A curve of corrections for the various burette readings should be drawn.

You may assume that 1 gram of water occupies a volume of 1 c.c.

EXPT. 22.—*To fill the burette with dry air.*—The burette having been carefully dried by gently heating and drawing air through it, replace it on the stand, fix it firmly in position, and re-attach the tubing. Pour clean dry mercury into the reservoir by the help of a suitable funnel. Care must be taken to remove any air which may have become entangled in the mercury in the pressure tubing.

The stopcock A (which should previously have been *slightly* greased) being opened, raise the reservoir R till the mercury almost reaches to the stopcock. If the reservoir is then slowly lowered, the air drawn into the burette will be dried by passing over the calcium chloride.

Bind a thermometer T on to the burette by means of some thin copper wire. After a few minutes read the thermometer, and observe the barometric pressure. When both of these are recorded, close the stopcock and carefully bind it in position by copper wire. The burette reading of the mercury surface having been recorded, you know the volume of dry air (at a known temperature, and subjected to the observed atmospheric pressure) which is contained above the mercury surface in the burette.

EXPT. 23.—*To subject the air contained in the burette to various pressures.*—This can be done by raising the reservoir to various heights. If we measure the pressures in centimetres of mercury, the pressure to which the air contained in the burette is subjected at any instant is equal to P, the barometric pressure (measured in cms. of mercury), *plus* the difference in level, in cms., between the surface of the mercury in the reservoir and of that in the burette.

The reservoir must be raised or lowered slowly, since the temperature of the air in the burette will be altered by any sudden compression or expansion. The readings to be taken at the present stage are :—

(1.) The burette graduation which corresponds to the surface of the contained mercury. (2.) The position of the mercury surface in the reservoir; this is obtained by noting the division on the centimetre scale which corresponds to the meniscus of the mercury on the gauge tube.

Make out a table in your observation book similar to the following—

Temperature of air = ...
Barometric pressure (in cms. of mercury) = . . .

Mercury surface in Burette.	Mercury surface in gauge tube, stopcock open.	Mercury surface in gauge tube, stopcock closed.	Head of Mercury.	Total pressure (p).	Volume of air contained in Burette (v).	pv.

You can now fill in columns 1 and 3 as your observations are made. After the reservoir has been raised as high as possible, readings having been taken for each successive increment of 20 cms. in its elevation, similar readings must be taken as the reservoir is lowered.

EXPT. 24.—*To find the head of mercury.*—When the above readings have been finished, and columns 1 and 3 completely filled up, open the stopcock at the top of the burette, and raise the reservoir so that the mercury surface in the burette successively occupies the exact positions which you have registered in column 1. Read off the corresponding positions of the mercury surface in the gauge tube. Since the burette is open to the atmosphere, the pressure at both mercury surfaces must be equal, and therefore both are exactly level. Record the readings which you thus take in column 2.

It is obvious that the difference between corresponding values in columns 3 and 2 will give the head of mercury, to the pressure of which, in addition to that of the atmosphere, a volume of air v (determined from the corresponding reading in column 1, together with the previously constructed correction curves) is subjected. The total pressure, p, is obtained by adding the barometric pressure, P, to the head of mercury. The remaining columns in the table can now, therefore, be filled in, the last column being obtained by multiplying the volume of the air in each instance by the total pressure to which it is subjected.

It will be noticed that the values in the last column agree to within an amount comparable with the magnitude of the unavoidable experimental errors.

Hence, at a constant temperature, the product of the volume of a given mass of gas, into the pressure to which it is subjected, remains constant as the pressure and volume are varied.

This is the celebrated generalisation known as **Boyle's Law.** It may also be written

$$pv = \kappa.$$

Take a piece of squared paper, and plot a curve exhibiting the relation between p and v. It is customary to plot the values of v horizontally (as abscissæ) and the corresponding values of p vertically (as ordinates). The student should accustom himself to this convention as soon as possible, as its disregard may sometimes lead to misapprehensions.

ACD, Fig. 46, is a graphical representation of the equation

$$pv = \kappa.$$

Thus, let us suppose that we start with a volume v of a gas equal to 5, using any arbitrary unit of volume, and that the pressure to which this gas is for the time subjected is also equal to 5, in arbitrary units. Then the condition of the gas is represented by the point C. If now the volume of the gas is reduced to 2·5, the pressure will be increased to 10.

The curve represented in Fig. 46 is called by mathematicians a Rectangular Hyperbola.

Isothermal.—According to the conventions previously explained, the relation between the pressure and the volume of a given mass of gas maintained at a constant temperature may be represented to a first approximation by a curve such as ACD, Fig. 46. Such a curve is called an isothermal of the gas. It may be as well to state here, what will be discussed more fully at a later period, that no gas exactly obeys Boyle's Law. The so-called permanent gases, such as hydrogen, helium, nitrogen, oxygen, &c., obey Boyle's Law very approximately at ordinary temperatures, whilst a certain amount of divergence may be noted in the case of carbonic acid and sulphurous acid gases under similar conditions. As a general rule, it may be stated that the higher the temperature of a gas is, the more nearly will it obey Boyle's Law.

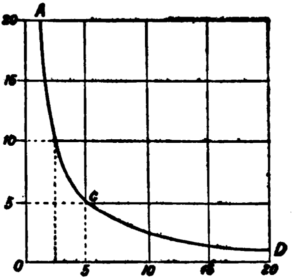


FIG. 46.—Isothermal of a perfect gas.

Perfect Gas.—A gas which obeys Boyle's Law is termed a perfect gas. From what has already been said, it will be seen that actual gases can only be considered as approximating more or less closely to the properties of a perfect gas.

Pure dry atmospheric air, oxygen, nitrogen, and hydrogen obey Boyle's law very closely at ordinary temperatures provided that the pressure varies only by a few atmospheres; hence they may be considered to be perfect gases. When one of these gases is enclosed in a vessel, and the temperature of the gas is raised, its pressure remaining constant, the volume of the gas increases. Let the initial temperature of the gas be 0° C. (*i.e.*, the temperature of melting ice), and let its volume at this temperature be equal to V. While the pressure is maintained constant, let the temperature be raised to 100° C. (*i.e.*, the temperature of water boiling under standard conditions), and let v be the consequent increase in the volume of gas. Then, since one cubic centimetre at 0° will obviously expand by the same amount as any other cubic centimetre, v will be proportional to V, and therefore v/V will be a constant; if this is divided by 100 (*i.e.*, the rise in temperature), we obtain **the increase in volume of each unit volume at 0° C. per degree rise of temperature, when the pressure is kept constant.** This quantity is called the **coefficient of expansion of the gas at constant pressure.**

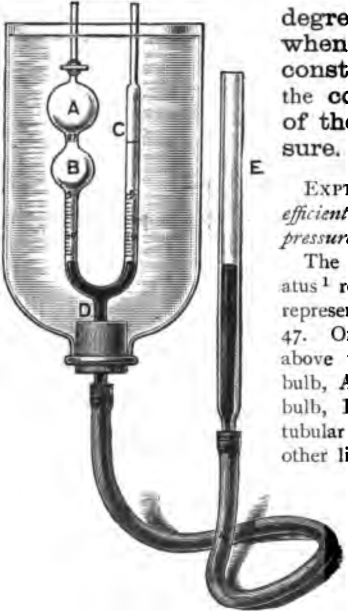


FIG. 47.—Apparatus for determining the coefficient of expansion of a gas at constant pressure.

EXPT. 25.—*To determine the coefficient of expansion of air at constant pressure.*

The essential details of the apparatus[1] required for this experiment are represented diagrammatically in Fig. 47. One limb of a U-tube, closed above with a stop-cock, comprises a bulb, A, of 27 c.c. capacity, a lower bulb, B, of 9 c.c. capacity, and a tubular portion graduated in c.cs.; the other limb, C, is tubular. Both limbs have corresponding graduations, as represented in the diagram. The stop-cock must be lubricated with a little burnt black or white (not red) rubber; this is the only lubricant that will stand the temperature of boiling water. The U-tube has a T-joint at D, which is connected by means of flexible pressure tubing with a glass tube, E. The U-tube is surrounded by a glass vessel which can be filled with water, to act as a constant temperature bath.

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[1] This apparatus, mounted on a suitable stand, can be obtained from the West London Scientific Apparatus Co., Premier Place, Putney, S.W.

The stop-cock above A being opened, mercury is poured into E till it rises in both limbs of the U-tube. The stand carrying the apparatus (not shown in Fig. 47) is provided with levelling screws; these are adjusted until the mercury stands at corresponding graduations in the two limbs. Subsequently, whenever the mercury stands at corresponding graduations in the two limbs, the pressure of the air in A will be equal to the atmospheric pressure. The tube E is next lowered till the mercury just forms a seal at the bottom of the U; by the aid of a bicycle pump air is pumped for some time through a drying tube containing calcium chloride and soda lime, and then through the bulbs A and B, escaping past the mercury seal into the tube C. Next, remove the pump, but leave the drying tube connected with the bulb A. Raise E till the mercury stands at the graduation between the two bulbs A and B, add plenty of ice to the water in the bath, and, when the whole has reached the temperature of melting ice, close the stop-cock above A. Twenty-seven c.cs. of pure dry air at 0° C. have now been enclosed at atmospheric pressure; hence $V=27$ c.cs.

Remove the unmelted ice, syphon off the cold water, and fill the bath with boiling water. In order to keep the water boiling, blow steam through it by means of a rubber tube the end of which dips down nearly to the bottom of the bath. When the bubbles of steam rise through the water without collapsing, the water is at its boiling point. Next lower E till the mercury stands at corresponding graduations in the two limbs of the U-tube; the enclosed air is now at atmospheric pressure, and the increase in its volume can be accurately read off from the graduation below B at which the mercury stands. This gives us v. Hence, determine the value $v/100V$.

The following *corrections* may be applied:

(*a*) Read the barometer, and use the true boiling point of water under the observed pressure, in place of 100° (see p. 27).

(*b*) Apply a correction for the expansion of the glass vessel.

Using this apparatus, the value obtained for the coefficient of expansion of air at constant volume should not differ by more than about 1 per cent. from $1/273$. Other perfect gases can be used in place of air, and these all will be found to have the same coefficient of expansion.

We can now determine some valuable relations by the aid of Fig. 48. In this we may suppose that the curve ABC represents the relation between the pressure and volume of a certain quantity of air when maintained at the temperature of melting ice. Let us suppose that the volumes are measured in c.cs., and the pressures in any arbitrary units. Then we see that when subjected to a pressure 20, the air occupied a volume of 20 c.cs. The increase in volume of 1 c.c. of air, when heated, under constant pressure, from the temperature of melting ice to that of boiling water, has already been determined. Hence we can calculate the increase in volume of 20 c.cs. under the same conditions. You may assume for the present that the increase in volume occurring when a gas is heated, is independent of the value of the constant pressure to which it is subjected.

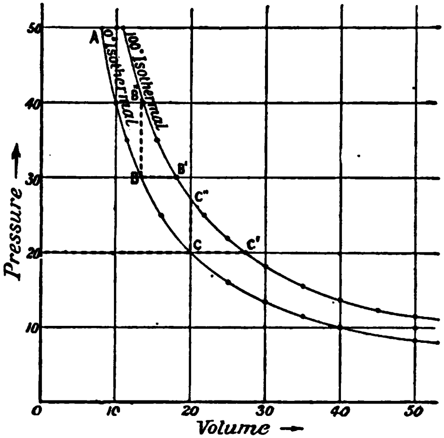

FIG. 48.—Isothermal of a perfect gas.

Now a horizontal line drawn through 20 will obviously represent all the points on Fig. 48 for which the pressure is constant and equal to 20. If, therefore, we mark off along this line a distance CC′ equal to the increment in volume of 20 c.cs. of air when heated from the temperature of melting ice to that of boiling water, C′ will be a point on the isothermal for the air, at a temperature which we may define as 100° C. This isothermal may be drawn in the same way as the first one, remembering that the volume of the air multiplied by the pressure to which it is subjected remains constant. We now have an isothermal for air at the temperature of melting ice (0° C.) and one for air at the boiling point of water (100° C.). We can divide the distance CC′ into 100 equal parts, and if the diagram had been drawn on a larger scale we might have drawn isothermals through each of these points. Then, if we number these isothermals consecutively as 0°, 1°, 2°, 3° . . . . 99°, 100°, we have the following method of measuring temperature.

A quantity of air is taken at 0° C., and the increase in its volume, when it is heated at constant pressure to 100° C., is noted. Call this increment δ. If this air is found at any subsequent period to occupy a volume greater by x than its initial volume at 0°, the pressure being equal to that at the beginning of the experiment, then the temperature is equal to

$$\left(\frac{x \times 100}{\delta}\right)^{\circ} \text{C.}$$

It will have been noted that, in the experiment last described, a mercury thermometer was not used. This was arranged intentionally, since, as previously pointed out, the most reliable method of measuring temperature is in terms of the expansion of gases. We have now arrived at a method of measuring temperature which is quite independent of the use of a mercury thermometer.

In obtaining the boiling point of an air thermometer, similar precautions and corrections to those already described in connection with a mercury thermometer are necessary.

General Equations to the Isothermals of a Perfect Gas.—Let

$$pv = \kappa$$

be the equation to the isothermal of a perfect gas at 0° C.

Let us suppose that a particular volume v_1 of gas at a temperature 0° C., and a pressure p_1, is heated to 100° C., the pressure meanwhile remaining constant. Let the consequent increase in volume of the gas be denoted by v_2. Then as long as the temperature of the gas remains at 100°, the product of its volume into the corresponding pressure will remain constant, and equal to $p_1(v_1 + v_2)$. Hence, if p, v, now denote *any* corresponding values of the pressure and volume of this quantity of gas at 100°, we have

$$pv = p_1(v_1 + v_2) = p_1v_1\left(1 + \frac{v_2}{v_1}\right).$$

Let $\frac{v_2}{v_1} = 100a$, so that a represents the increase in volume of 1 c.c. of gas, when heated from 0° to 1° C., or $\frac{1}{100}$ of the increase in volume of 1 c.c. of the gas when heated from 0° to 100° C.

Then $$1 + \frac{v_2}{v_1} = 1 + 100a.$$

Also $$p_1v_1 = \kappa.$$

$$\therefore\ pv = p_1v_1(1 + 100a) = \kappa(1 + 100a).$$

If the temperature had been t° C. instead of 100° C., v_1 would have been increased by v'_2, where

$$\frac{v_2'}{v_1} = ta.$$

Hence the equation, to the isothermal to the gas at t° C., is

$$pv = \kappa(1 + at).$$

You have already obtained a value for a. As the result of experiments to be presently described, Regnault found a to be equal to $\frac{1}{273}$, or ·003665.

a is termed the coefficient of expansion of a gas at constant pressure.

Increase in pressure of a gas, the volume of which is maintained constant whilst its temperature is raised.

Referring to Fig. 48, it will be seen that the line CC″ is equal in length to CC′. Now since the gas at C is at a temperature of 0° C., whilst at C″ it is at 100° C., the volume in both cases being equal to 20, CC″ represents the increase in pressure of the gas when heated from 0° to 100° C., the volume remaining constant.

Let us take any other point on the zero isothermal, B for instance, corresponding to a volume 13·3 and a pressure 30. Then BB′ = 4·9, BB″ = 11.

Then, increase in volume of 1 c.c. of gas at 0° C., when heated to 100° under a constant pressure 30, $= \frac{BB'}{13 \cdot 3} = \frac{4 \cdot 9}{13 \cdot 3} = \cdot 36$.

Also, the ratio of the increase of pressure, 11, to the initial pressure, 30, when the gas is heated from 0° to 100° C. $= \frac{11}{30} = \cdot 36$.

If a given quantity of a gas is heated from 0° to 1° C., its volume remaining constant, then the ratio of the increase of pressure to the initial pressure is termed the coefficient of increase of pressure of the gas.

This quantity is also sometimes termed the coefficient of expansion of the gas at constant volume. But as the gas is, by the nature of the case, not allowed to expand, this term is somewhat misleading. It is best to use the term given above, or the simple contraction "pressure coefficient of the gas."

In the case of a perfect gas, the pressure coefficient is numerically equal to the coefficient of expansion at constant pressure.

We have just found this to be the case from measurements made on the isothermals given in Fig. 48. It will now be shown that this is so, from the equations to these isothermals.

We have seen that if

$$pv = \kappa$$

is the equation to the 0° C. isothermal of a gas, then the t° C. isothermal will be represented by the equation

$$pv = \kappa(1 + at)$$

where a is the coefficient of expansion at constant pressure.

If we take a volume v_1 of a gas, subjected to a pressure p_1, at 0° C., and raise its temperature to 100° C., its pressure being increased by p_2, in order to maintain its volume constant, then we shall have the 100° isothermal represented by

$$pv = (p_1 + p_2)v_1 = p_1 v_1 \left(1 + \frac{p_2}{p_1}\right).$$

Let $\frac{p_2}{p_1} = 100\beta$, where β is the pressure coefficient of the gas, as previously defined. Then since

$$p_1 v_1 = \kappa,$$

we have for the equation of the 100° isothermal

$$pv = \kappa(1 + 100\beta).$$

Similarly, the t° C. isothermal will be represented by

$$pv = \kappa(1 + \beta t).$$

But we have already found the t° C. isothermal to be represented by

$$pv = \kappa(1 + \alpha t).$$

$$\therefore\ \alpha = \beta.$$

i.e., the coefficient of expansion of a perfect gas at constant pressure is equal to the pressure coefficient of that gas.

Volume of a Gas when cooled below 0° C.—In accordance with the method of measuring temperature which we have adopted, a cubic centimetre of gas, if cooled to -1° C., its pressure remaining constant, would have its volume decreased by α, or $\frac{1}{273}$ c.c. If cooled to -2° C. under similar conditions, its volume would be decreased by $\frac{2}{273}$ c.cs. Similarly, if cooled to -273° C., its volume would be decreased by $\frac{273}{273} = 1$ c.c.; *i.e.*, its volume would be diminished to zero. Passing over, for the moment, the difficulty of conceiving that anything should be capable of being reduced to occupy no space, we can at least agree that no further diminution of volume could occur through cooling.

Absolute Zero of Temperature.—For the reasons just mentioned, -273° C. is termed the absolute zero of temperature. In spite of the difficulties which underlie this reasoning, we must adopt, for the present, the results arrived at. A satisfactory justification of our procedure will be forthcoming when we come to study the kinetic theory of gases (Chap. XIII.).

Absolute Temperature.—The absolute temperature of any body is its temperature measured from the absolute zero. Thus a temperature of 50° C. is equivalent to an absolute temperature of $50 + 273 = 323^\circ$, and, generally, the absolute temperature is obtained by adding 273° to the ordinary centigrade temperature.

Of course, the absolute zero could be expressed in terms of Fahrenheit degrees, and the absolute temperature of anything could thus be given in terms of the same unit.

To express the equation of the Isothermals of a

Perfect Gas in terms of its absolute temperature.—As previously shown, the isothermals of a perfect gas are represented by the equation

$$pv = \kappa\left(1 + \frac{t}{273}\right) = \frac{\kappa}{273}(273 + t).$$

Further, $273 + t$ is equal to the absolute temperature of the gas. Let $273 + t = \mathrm{T}$; then since $\frac{\kappa}{273}$ is a constant, which we may denote by R, we have the following simple expression for the isothermals of a perfect gas:—

$$pv = \mathrm{RT}.$$

It may be well here to work a few examples relative to the expansion of gases.

Example.—1. A certain quantity of gas occupies a volume of 500 c.cs. at 15° C. under atmospheric pressure. What volume will it occupy at 200° C. under the same pressure?

Let p represent the atmospheric pressure. Then, since the initial and final temperatures, when measured from the absolute zero, are respectively equal to $273 + 15 = 288$ and $273 + 200 = 473$, we have, if v equals the final volume which we are required to determine

$$p \times 500 = \mathrm{R} \times 288.$$

$$\therefore \frac{\mathrm{R}}{p} = \frac{500}{288}.$$

$$pv = \mathrm{R} \times 473.$$

$$\therefore v = 473 \times \frac{\mathrm{R}}{p} = 473 \times \frac{500}{288} = 821 \text{ c.cs.}$$

The student is particularly warned against attempting to obtain the solution of problems such as the above by multiplying the initial volume by $\{1 + a(t_2 - t_1)\}$ where t_1 and t_2 are the initial and final temperatures of the gas; unless, indeed, the initial temperature is zero. The value obtained as a solution of the above problem, when this latter method is used, is equal to 839 c.cs., which differs considerably from the correct value.

2. A certain quantity of gas occupies a volume of 300 c.cs. at 25° C., under atmospheric pressure. At what temperature will

the same gas occupy a volume of 200 c.cs. under an equal pressure?

$$p \times 300 = R(273 + 25) = R \times 298. \therefore \frac{p}{R} = \frac{298}{300}$$

$$p \times 200 = RT.$$

$$T = 200 \times \frac{p}{R} = 200 \times \frac{298}{300} = 198{\cdot}6.$$

Hence the absolute temperature required is 198·6°, which corresponds to 198·6 − 273 = − 74·4° C.

3. A quantity of gas, collected in a graduated vessel over mercury, is observed to occupy 215 c.cs. The surface of the mercury inside the containing vessel stands 3·5 cms. above that of the surrounding mercury. The temperature of the room is 20° C., and the barometric pressure is equal to 758 mm. What volume would the collected gas occupy at 0° C. when subjected to a normal pressure of 760 mm. of mercury?

Pressure to which gas is subjected = 75·8 − 3·5 = 72·3 cm. of mercury.

Volume of gas, under above pressure, and at 20° C. = 215 c.cs.

Absolute temperature of gas = 273 + 20 = 293.

Substituting in equation

$$pv = RT,$$

we have

$$72{\cdot}3 \times 215 = R \times 293.$$

$$\therefore R = 72{\cdot}3 \times \frac{215}{293}.$$

Under the conditions subsequently specified

$$p = 76{\cdot}0, \quad v = ? \quad T = 273.$$

$$76{\cdot}0 \times v = R \times 273.$$

$$\therefore v = \frac{273}{76{\cdot}0} \times R = \frac{273}{76{\cdot}0} \times \frac{72{\cdot}3 \times 215}{293}$$

$$= 190 \text{ c.cs.}$$

Further problems will be found at the end of the chapter.

EXPT. 26.—*To determine the pressure coefficient of a gas.*—In order to determine the pressure coefficient of a gas, it is necessary to enclose a quantity of pure dry gas at the temperature of melting ice and at a known pressure, P, and then to observe the increase of pressure p which must be applied to the gas in order that its volume may remain unchanged when the temperature rises to that of boiling water (*i.e.*, 100° if the atmospheric pressure is normal). Then the pressure coefficient is equal to $p/100$ P. Since the pressures occur only in the form of a ratio, the value of the pressure coefficient will be the same whatever unit may be used in measuring P and p, provided that both these quantities are measured in terms of the same unit. It is most convenient to measure P and p in centimetres or millimetres of mercury, and to arrange that P is equal to the barometric pressure.

A piece of apparatus[1] for measuring the pressure coefficient of a gas is represented in Fig. 49. A cylindrical bulb, A, of about 200 c.cs. capacity is closed above with a stop-cock, and connected below by means of flexible pressure tubing with a movable tube, C. The stop-cock must be lubricated with a little burnt black or white (not red) rubber.

To commence an experiment, pour a very small quantity of mercury into C, so that it just forms a seal at the lower part of the pressure tube. Open the stop-cock and force air (or the gas to be experimented with) through A after it has traversed a drying tube containing calcium chloride and soda lime. While the drying tube is still connected with the bulb, pour more mercury into C, and raise C till the mercury stands at a mark B in the glass tube below A. Next place water and plenty of ice in the bath surrounding A, stir well, and finally close the stop-cock above A. A volume of pure dry air at 0° C. and at atmospheric pressure has now been enclosed. Read the barometer, and thus obtain P. The cursor D should be adjusted until its lower edge just coincides with the surface of the mercury in the tube C, and the corresponding reading on the scale at the side of C should be observed.

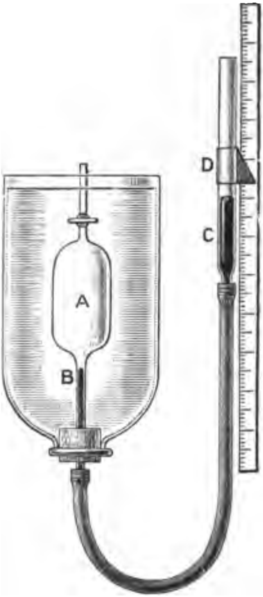

FIG. 49.—Apparatus for determining the pressure coefficient of a gas.

Next raise the tube C until the mercury rises well within the bulb A; this is done in order that, when the temperature of the bath is raised, the air shall not be able to expand into the rubber tube which connects A with C.

Remove the ice, syphon off the cold water from the bath, and fill the latter with boiling water. Keep the water boiling by blowing steam through it; when the bubbles of steam rise without collapsing, the water is at its boiling point. When this condition is attained, adjust C until the mercury stands at the mark B as before; then, by the aid of the cursor D, observe the reading corresponding to the mercury surface in C; subtracting from this the scale reading previously observed, we obtain the value of the increase of pressure p.

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[1] This apparatus, mounted on a suitable stand, can be obtained from the West London Scientific Apparatus Co., Premier Place, Putney, S.W.

The following corrections may be applied:—

(*a*) The mercury in the tube below A, being hotter than that in the tube C, will be less dense. Error due to this cause may be eliminated by finally taking the reading of the mercury surface in C when the stop-cock is open and the water in the bath is boiling, and using this instead of the scale reading obtained before the bath was heated.

(*b*) Find the true temperature at which water boils under the observed barometric pressure (p. 27).

(*c*) Allow for the expansion of the glass vessel.

Let V be the (unknown) volume of the vessel at 0°; then at 100° C. the volume will be $V(1 + 100g)$, where g is the coefficient of expansion of the glass. Thus at 100° C, the volume of the gas was $V(1 + 100g)$, and its pressure was $P+p$. In order to reduce its volume to the initial value V, some slightly higher pressure $P+p'$ would be necessary; and by Boyle's law

$$(P+p)V(1+100g) = (P+p')V,$$

$$\therefore\ (P+p)(1+100g) = P+p',$$

$$\text{and}\ \ p' = 100gP + p(1+100g),$$

$$\therefore\ \text{True pressure coefficient}$$

$$= \frac{p'}{100P} = g + \frac{p(1+100g)}{100P}.$$

Determination of the pressure coefficient of a Gas. —Regnault's Experiments.—A bulb A, Fig. 50, was connected by means of a narrow tube BE with the wide vertical tube FH. This latter tube was put in connection with another vertical tube, JI, by means of the metal connection HI, possessing a stop-cock K, by which the interior of both tubes could be put in connection with the external air. The bulb A, which had a capacity of about 700 c.cs., was first carefully dried, and then, while surrounded by melting ice, was filled with the dry gas to be experimented on. Mercury was poured into the tube JI at J, till the surface stood at *a* in the tube FH, the surface in JI being on the same level, since the side tube Cp afforded a means of communication with the external air. The height of these surfaces was read by means of a cathetometer. This instrument consists of a telescope provided with cross-wires in the eyepiece, and mounted on a vertical pillar (Fig. 51). The telescope can be raised or lowered, whilst its axis remains horizontal. It was initially adjusted, so that the images of the mercury

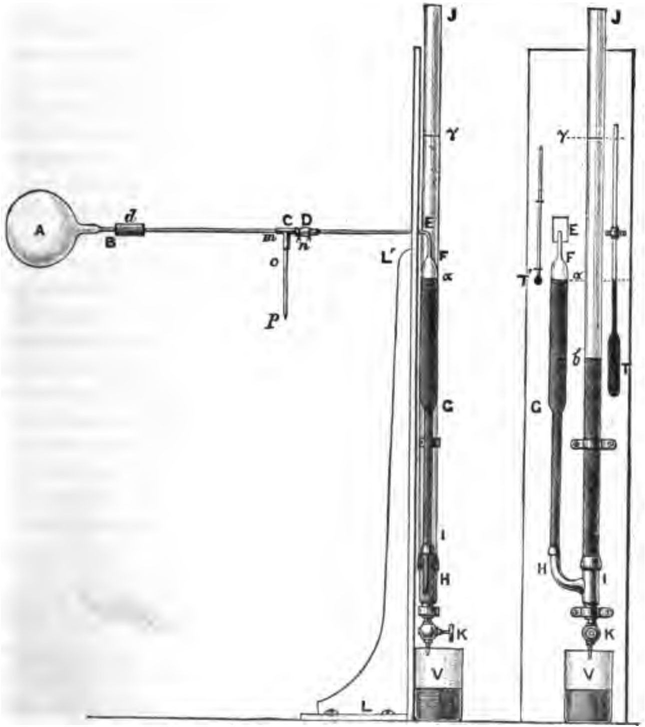

Fig. 50.—Regnault's constant volume air thermometer. (P.)

surface coincided with the intersection of the cross wires. Any subsequent change of level of the mercury surfaces could be exactly measured by raising or lowering the telescope till the image of the mercury surface again coincided with the cross wires, and observing the vertical distance through which the telescope had been moved.

The tube CP was then sealed off at P. A certain quantity of dry gas, at a temperature of 0° C., and at atmospheric pressure, was thus contained in the apparatus.

The bulb A was then heated in a steam jacket, mercury being poured into the tube JI so as to always keep the surface in FH at its initial position a. When it was seen that no further addition of mercury was necessary, the height of the surface in JI, (which stood at γ,) was read by means of a cathetometer (Fig. 51).

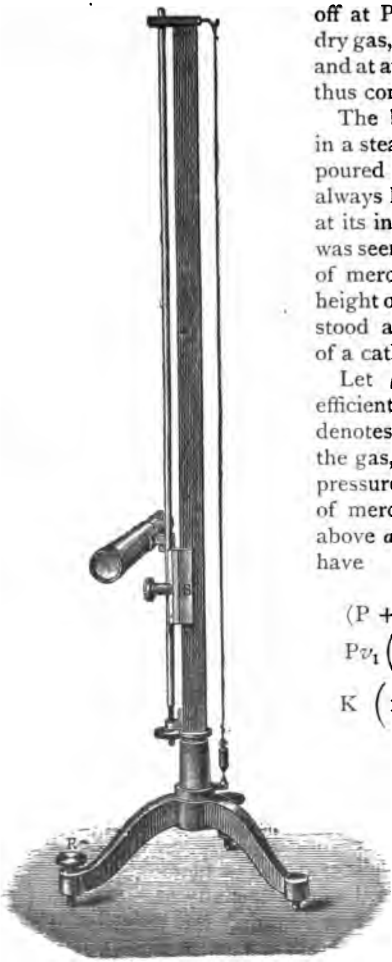

FIG. 51.—Cathetometer.

Let β be the pressure coefficient of the gas. Then if v_1 denotes the initial volume of the gas, P being the barometric pressure measured in centimetres of mercury, and the height of γ above a is taken as p cms., we have

$$Pv_1 = K.$$

$$(P + p)v_1 = K(1 + 100\beta).$$

$$Pv_1\left(1 + \frac{p}{P}\right) = K(1 + 100\beta).$$

$$K\left(1 + \frac{p}{P}\right) = K(1 + 100\beta).$$

$$\frac{p}{P} = 100\beta.$$

$$\therefore \beta = \frac{p}{100P}.$$

Experiments were also made when the initial pressure was either greater or less than the atmospheric pressure.

In the above reasoning we have neglected two points which must be taken into account for accurate work.

1. The temperature of the air in the bulb A is slightly different from that of the air in the connecting tube BE and the top of the vertical tube E*a*. Only a small error is introduced on this account, since the volume of air in A is relatively large in comparison with that in BE and E*a*.

2. The glass bulb expands when heated. As, however, the expansion of glass is less than $\frac{1}{100}$ of that of the air, this necessitates only a relatively small correction.

Jolly's Apparatus.—Some inconvenience is occasioned when using Regnault's air thermometer by the necessity of pouring mercury into the tube JI, or removing it by means of the stop-cock K (Fig. 50). In Jolly's thermometer, these inconveniences are overcome by connecting the tubes BD and EC (Fig. 52) by means of a piece of indiarubber pressure tubing. The mercury surface can be maintained at B, whatever may be the temperature of the air in A, by simply raising or lowering the tube EC.

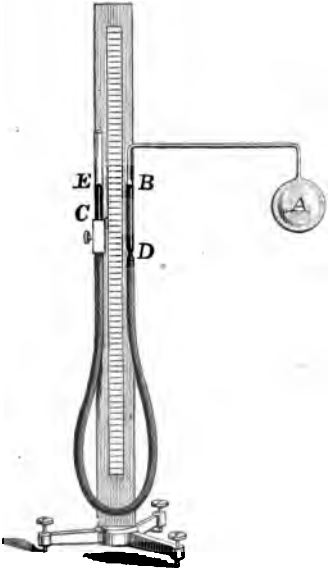

Fig. 52.—Jolly's constant volume air thermometer. (P.)

The Expansion of Gases under Constant Pressure. Regnault's Apparatus. — Whenever the mercury surfaces in the tubes FH and JI, Fig. 50, are level with each other, the pressure of the air contained in A is equal to the atmospheric pressure.

If the mercury surfaces are level when the bulb A is surrounded by melting ice, then as the air in A is heated, the surface in FH will be forced downwards, whilst that in JI will be raised. In order to keep the surfaces level with each other, mercury must be drawn off from K.

It follows that the whole of the air will no longer be contained by A; part of it has expanded into the tube FH, and the increase of volume can therefore be directly observed.

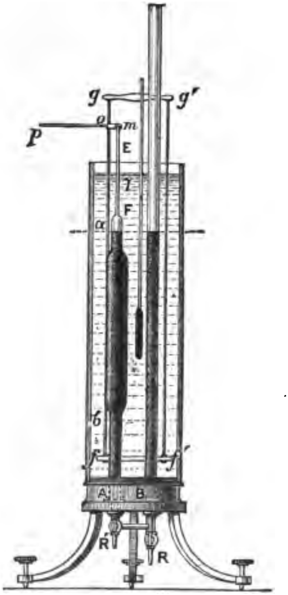

FIG. 53.—Regnault's constant pressure air thermometer.

(A bulb, similar to A, Fig. 50, was joined on at *p*). (P.)

It is most important that the temperature of the air in FH should be accurately known. In order to accomplish this the two tubes containing the mercury were entirely surrounded by a water bath (Fig. 53).

Regnault considered the results given by this apparatus to be less trustworthy than those obtained by the use of the constant volume apparatus.

Gas Laws.—The results of Regnault's experiments were as follows:—

1. All permanent gases, such as oxygen, nitrogen, hydrogen, possess coefficients of expansion at constant pressure which are approximately, but not exactly, equal. The mean value of this coefficient is ·003665.
2. The coefficient of expansion of a gas at constant pressure, is approximately, but not exactly, equal to its pressure coefficient.
3. In the case of hydrogen, the coefficient of expansion at constant pressure is independent of the pressure. In the case of other gases, the coefficient of expansion increases slightly as the pressure is decreased.
4. The properties of gases, such as SO_2 and CO_2, approach more nearly to those of perfect gases, in proportion as their pressures are diminished and their temperatures are raised.

Air Thermometers.—Since Regnault's experiments established the validity of the reasoning employed on pp. 100 and 104, especially as regards hydrogen, the equation to the isothermals of a perfect gas may be written

$$pv = \mathrm{RT},$$

where T is the absolute temperature of the gas, *i.e.* $273 + t^\circ$ C.

Hence, using the constant volume apparatus (Fig. 50), the temperature of the contained air may be determined from an observation of its pressure.

Callendar's Compensated Constant Pressure Air Thermometer.—Since the gas thermometer is the ultimate standard in all temperature measurements, it is exceedingly important that all thermometers used in accurate research should be compared with it. Through neglect of this precaution much otherwise irreproachable experimental work has sometimes been rendered quite valueless. Prof. Callendar has devised the form of air thermometer represented diagrammatically in Fig. 54.

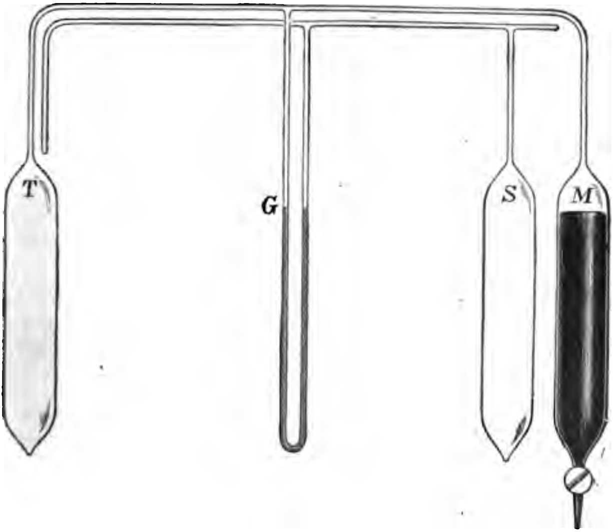

FIG. 54.—Callendar's compensated air thermometer. (P.)

The thermometer bulb T is connected directly with the mercury tube M, and indirectly, through a sulphuric acid pressure gauge G, with the bulb S. This latter bulb is filled with dry air and is constantly surrounded by melting ice. The pressure in S is therefore constant, and is independent of the barometric pressure. T is placed in melting ice, and the level of the mercury in M is adjusted till the gauge G shows the pressure in T to be equal to that in S. The tube M having been graduated and calibrated, the temperature of the air in T, when it is necessary to bring the mercury surface in M to any other level in order to preserve equality in the pressures of the air in T and S, may be calculated.

Errors due to the unknown temperature of the air in the tube connecting T and M, is eliminated by placing beside it a tube of the same dimensions, but connected with S.

Prof. Callendar claims that with the above form of apparatus a temperature as high as 450° C. can be measured to within $\frac{1}{10}$ degree, and that when the dimensions of the various parts are properly adjusted, the results are very trustworthy.

PROBLEM. Obtain a formula connecting the volume of the air in the mercury tube M of Callendar's air thermometer with the temperature of the air in T.

Let T = the absolute temperature of the air in the bulb T (Fig. 54), and let v_1 = its volume.

Let $T_0 (=273)$ = the absolute temperature of the air above the mercury in M, and let v_2 = its volume.

Let T_1 = the absolute temperature of the air in the connecting tube, and let v_3 = its volume.

Let m = the mass of the air contained in T, M, and the connecting tube.

The mercury in M is adjusted so that the air throughout the apparatus is all at the same pressure.

Let ρ represent the density (*i.e.* mass of unit volume) of air at 0° C., and at a pressure equal to that of the air in S; then the air in the bulb T, which occupies a volume of v_1 c.cs. at the temperature T, would occupy a volume of $\frac{v_1 T_0}{T}$ at an absolute temperature T_0 (0° C.).

$$\therefore \text{ Mass of air in the bulb T} = \frac{\rho T_0}{T} v_1.$$

Similarly mass of air in M $= \rho v_2$, and mass of air in connecting tube

$$= \frac{\rho T_0}{T_1} v_3.$$

$$\therefore \ \rho T_0 \left(\frac{v_1}{T} + \frac{v_2}{T_0} + \frac{v_3}{T_1} \right) = m.$$

Let $v_4 =$ the volume of the bulb S, and v_5 the volume of the compensating tube which lies alongside the tube connecting T and M. Then mass of air contained by S and compensating tube

$$= \rho T_0 \left(\frac{v_4}{T_0} + \frac{v_5}{T_1} \right).$$

If the mass of air contained by T, M and the connecting tube = mass of air contained by S and compensating tube, we have

$$\frac{v_1}{T} + \frac{v_2}{T_0} + \frac{v_3}{T_1} = \frac{v_4}{T_0} + \frac{v_5}{T_1}.$$

Further, if the volume v_3 contained by the connecting tube, is equal to v_5, the volume contained by the compensating tube; and v_1, the volume of the bulb T is equal to v_4, the volume of S, we have

$$\frac{v_1}{T} + \frac{v_2}{T_0} = \frac{v_1}{T_0}.$$

$$\frac{v_1}{T} = \frac{v_1 - v_2}{T_0}$$

$$\therefore \ T = \frac{v_1 T_0}{v_1 - v_2}.$$

The student is recommended carefully to follow the above reasoning, as similar methods are often required in the solution of problems.

SUMMARY.

Boyle's Law.—The product of the pressure into the volume of a given mass of a **perfect gas** remains constant as long as the temperature of the gas is unchanged.

The Permanent Gases—Oxygen, Hydrogen, and Nitrogen, closely approximate in properties to perfect gases.

Isothermals.—A curve representing the relation between the pressure and volume of a gas at a constant temperature is termed an isothermal curve.

Coefficient of Expansion of a Gas at Constant Pressure.—The increase in volume of a quantity of gas occupying a volume 1 c.c. at 0° C., is equal to $\frac{1}{273}$ c.c. for each successive degree of temperature.

Absolute Zero.—If a perfect gas were cooled to − 273° C. its volume would be reduced to nothing. Hence $-273°$ C. is termed the absolute zero of temperature. No substance can possibly be cooled below the absolute zero.

Absolute Temperatures are measured from $-273°$ C., *i.e.*, by adding 273 to the Centigrade temperature.

The Equation to the Isothermals of a perfect gas may be written $pv = RT$, where T is the absolute temperature.

Pressure Coefficient.—When a gas is heated under such conditions that its volume remains constant, the ratio of the increase of pressure per degree Centigrade to the pressure of the gas at 0° C. is termed the pressure coefficient.

The value of the pressure coefficient is approximately, but not exactly, equal to $\frac{1}{273}$, the coefficient of expansion of the gas at constant pressure.

Air Thermometers.—The expansion of a gas at constant pressure may be used to measure temperature. The necessary arrangement is termed a constant pressure air thermometer.

A measurement of the increase of pressure which occurs when a gas is heated under such conditions that its volume remains constant may also be used to measure temperature. The necessary arrangement is termed a constant volume air thermometer.

Since the thermal expansion of a gas for a given rise of temperature is very great in comparison with the expansion of the containing vessel, an air thermometer is to be preferred above a mercury thermometer.

All mercury thermometers should be calibrated by comparison with an air thermometer.

Questions on Chapter V.

(1) Describe the experiments you would make to prove that for a gas at constant temperature pv is constant, p being the pressure and v the volume of the gas.

In a certain gas pv is observed to decrease slightly as the pressure rises. Show that the resistance to compression is less than it would be if Boyle's Law held.

(2) A barometer tube is filled with mercury up to within one inch of the top. After inversion the air expands and occupies 12 inches of the tube, and the mercury stands 27 inches in the tube above the level of the mercury in the trough. Find the true height of the barometer.

(3) When the height of the barometer is 76 cms., then the volume of a given mass of gas at 0° C. is 50 c.c.s., and when the temperature is raised to 100° C. and the pressure increased by that due to 27·8 cms. of

mercury, the volume remains unchanged; find the coefficient of change of pressure with temperature of the gas.

(4) Describe the apparatus required, and explain the mode of determining the coefficient of increase of pressure with change of temperature, of a mass of air occupying a constant volume.

(5) Define a perfect gas. How would you prove the accuracy of the statement that in a perfect gas $\frac{pv}{\mathrm{T}} =$ constant where p is the pressure, v the volume, and T the absolute temperature?

(6) Discuss the advantages and disadvantages of a constant volume air thermometer (*a*) as a standard of temperature, (*b*) as a convenient means of measuring temperatures.

(7) Describe carefully the experiments you would make to show that at constant volume the pressure of a given mass of gas is proportional to the absolute temperature.

(8) Describe carefully some method of measuring very low temperatures, such as $-120°$ C.

(9) How would you determine accurately the coefficient of expansion of a gas under constant pressure? A gram of air is heated from 15° C. to 60° C. under a pressure of 75 cms. of mercury. How much external work is done in the expansion?

Density of mercury = 13·6, $g = 981$ cm. per second.

(For last part of question, *see* Chap. XIII.)

(10) Describe the constant volume air thermometer. How would you use it to find the absolute zero of the air thermometer?

(11) Why is it necessary to have a good vacuum above the mercury in a barometer? Show how the atmospheric pressure could be obtained even from a barometer with air above the mercury, if the level in the cistern were adjustable, and if a suitably placed thermometer were also read.

(12) State concisely the characteristic properties of permanent gases, and sketch an apparatus for determining their coefficient of expansion at constant volume.

(13) Describe and explain the method of using some form of air thermometer.

(14) A mass of gas is warmed from 15° C. to 70° C. Calculate its final volume if it initially occupied 1,784 c.c.s.

(15) Describe the air thermometer and state its special advantages and disadvantages.

Explain clearly the meaning of absolute temperature on the air thermometer scale.

(16) State in words, and also in symbols, the two laws which, if a

gas obeys, it is called a "perfect gas," and explain clearly how the symbols represent the same laws as the words.

One pound of air at a temperature of 0° C., and at a pressure of 1,033 grams per sq. cm. has a volume of 0·3555 cubic metres. At what pressure will its volume be 403,700 c.c. if measured at a temperature of 27° C?

(17) Describe a form of air thermometer, and explain what measurements you would make to determine by it the temperature of a vessel of hot water. Give a brief account of the corrections to be applied.

Why is it better to define equal degrees of temperature by the air thermometer than by the mercury in glass thermometer?

(18) Describe an experiment to verify Boyle's Law for pressures less than the atmospheric pressure.

Some air is in the space above the mercury in a barometer, of which the tube is uniform. When the mercury stands at 29 inches in the tube the space above the mercury is 4 inches long. The tube is then pushed down into the cistern, so that the space above the mercury is only 2 inches long, and now the mercury stands at 28 inches. At what height would it stand in a perfect barometer?

(19) How may the coefficient of pressure increase of a gas at constant volume be determined?

A given volume of air is at 740 mm. pressure at 17° C. What is the temperature when its pressure is 1,850 mm.?

PRACTICAL.

(1) A narrow tube, closed at one end, has a short column of mercury near the other end. Investigate the elasticity of air by holding the tube with the open end (1) up, (2) down, and measuring the volume of air in each case. Specific gravity of mercury = 13·6, $g = 981$.

(2) Given a long narrow tube, closed at one end, introduce a short column of mercury, and graduate as a barometer, the readings being correct at 0°. Give a graphical table of temperature corrections on section paper.

(3) Compare a mercury and an air thermometer.

CHAPTER VI

CALORIMETRY—SPECIFIC HEATS OF SOLIDS AND LIQUIDS

In the previous chapters attention has been directed to some of the methods available for measuring temperature, and to certain changes which occur in the dimensions of solids, liquids, and gases when their temperatures are altered. We have not as yet found it necessary to make any assumptions as to the physical conditions which determine whether a body is hot or cold. Starting from the observed fact that a body may be hotter at one time than at another, we have investigated the consequent changes of dimensions, and have finally arrived at a satisfactory method of measuring temperature in terms of the volume and pressure of a quantity of gas, or, less satisfactorily, in terms of the volume occupied by an arbitrary quantity of mercury.

Quantity of Heat.—It now becomes necessary to make certain assumptions regarding the physical conditions which determine the temperature of a body. The necessity of these assumptions will be made clearer by the performance of the following experiment :—

Expt. 27.—Through a cork, selected to fit into the mouth of a large test-tube, bore a hole of such a size that a thermometer can just be pushed through it. Cut a small groove at the side of the cork, so as to form a channel for air to escape. Partially fill the test-tube with water, at a temperature of about 80° C., and insert the cork so that the thermometer bulb is immersed.

Partially fill a beaker with water at about 15° C. Support a second thermometer with its bulb immersed in this water, in the manner shown in Fig. 55. Write down the temperature of the water in the beaker, and then immerse the test-tube containing the warmer water, as shown in the figure. Stir the water in the beaker by moving the test-tube about in it. Write down the temperatures indicated by both thermometers at the end of each minute.

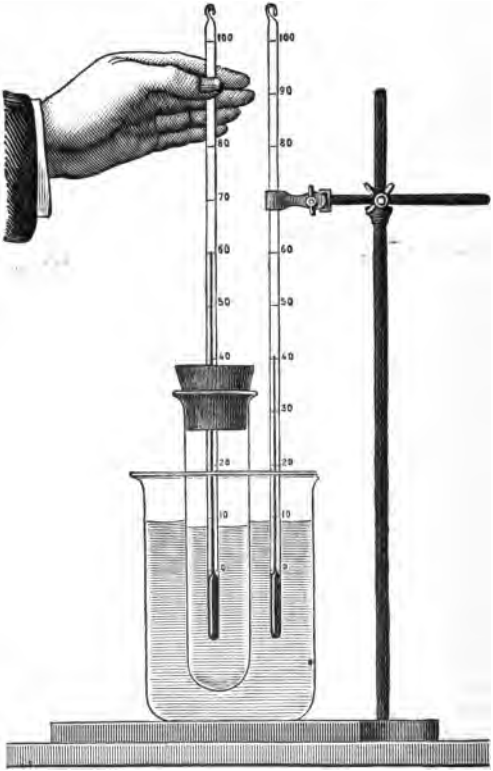

FIG. 55.—Apparatus for showing transference of heat from hot to cold water.

It will be noticed that at the commencement of the experiment the hot water in the test-tube cools somewhat rapidly, and after a time reaches a temperature which falls very slowly. On the other hand the water in the beaker rises in temperature, rapidly at first, and then more slowly, and after a time reaches a temperature nearly equal to that of the water in the test-tube. Write down the common temperature thus attained. If the thermometers are observed subsequently, it will be found that both indicate falling temperatures which are very nearly equal, the thermometer in the test-tube indicating a slightly higher temperature than that of the water in the beaker.

We now have observed the following facts :—

1. Two quantities of water, when placed in close connection with each other, tend to acquire the same final temperature. The temperature of the hot water falls, whilst that of the cold water rises.

2. The fall in temperature of the hot water is not necessarily equal to the rise in temperature of the cold water.

To explain these facts, we may assume that something has passed from the hot to the cold water, and that the temperature changes result from this transference. It is not *temperature* which has passed from one to the other, since the loss in temperature of the hot water is not necessarily equal to the gain in temperature of the cold water. We therefore assume that something else, which we call *Heat*, has been transferred. In parting with heat the temperature of the hot water is lowered, whilst a rise of temperature of the cold water results from the heat communicated to it.

It must be noticed that whereas the *temperature* of a body is directly observed, this passage of *heat* is only inferred. The value of this inference must be judged by its subsequent usefulness in explaining the phenomena attending the thermal changes of bodies.

We need not, at present, specify the precise nature of heat, further than to remark that as a body weighs no more when hot than when cold, heat is not a material substance. For many purposes it will suffice to assume heat to be a fluid that does not possess weight. A belief in the existence of this hypothetical fluid was at one time almost universal. The name given to it was *Caloric*. By assuming the existence of this fluid, we may explain most of the phenomena to be discussed in this and a few ensuing chapters.

It will, however, be found insufficient to account for many phenomena to be subsequently considered. The present state of our knowledge leaves little room for doubt that heat is really the energy of the moving molecules of a substance.

Hydrostatic Analogy.—Consider two cylindrical vessels, A, B (Fig. 56), joined by means of the horizontal tube CD, furnished with a stopcock E. Let us suppose that the stopcock E is closed, and that water is poured into A and B. Then if the water surface in A is at a higher level than that in B, water will flow from A into B when the stop-cock is opened, the transference continuing until the surfaces in the two vessels are in the same horizontal plane. This transference of water corresponds to the assumed transference of heat when two bodies at different temperatures are placed in thermal communication.

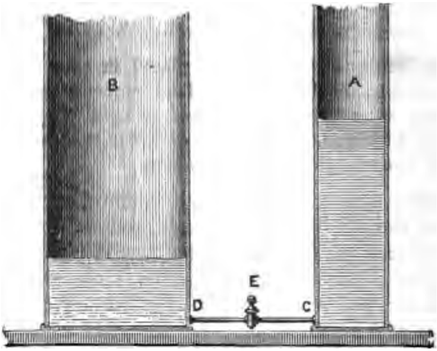

FIG. 56.—Apparatus illustrating the similarity between the flow of heat and the flow of water.

The difference in level of the two surfaces obviously corresponds to the difference of temperature of the bodies considered in the thermal problem.

It will be noticed that the *amount of water* which passes from A to B depends, not alone on the initial difference of level of the surfaces, but also on the sectional areas of the vessels.

Let us determine the amount of water which will flow from A into B.

Let a = sectional area of A, in sq. cms., so that a decrease in height of 1 cm. will correspond to a transference of a c.cs. from A into B.

Let b = sectional area of B.

,, h = initial difference in level of the two surfaces.

,, x = distance through which the surface in A falls when the stop-cock is opened.

,, y = distance through which the surface in B rises.

Then for the surfaces to be finally level, we have $h - x = y$.

Also, since the water which leaves A, equal to xa c.cs., flows into b, raising the surface there through y cms., we have

$$xa = yb. \quad \therefore y = \frac{xa}{b}.$$

$$h - x = \frac{xa}{b}. \quad \therefore x = \frac{bh}{a+b}.$$

Finally the volume of the water which flows from A into B

$$= xa = \frac{abh}{a+b}.$$

If $a = b$, then $y = x$, *i.e.*, the liquid rises as much in one vessel as it falls in the other.

If $a = 2b$, then $y = 2x$, *i.e.*, the water rises twice the distance in B that it falls in A.

We might call the quantities a and b the specific capacities of the vessels, per unit height.

EXPT. 28.—Take 100 grams of water in a beaker, and heat it to 60° C. Pour this into a beaker containing 100 grams of cold water, the exact temperature of which has been noted. Determine the temperature of the mixture when it has been thoroughly stirred. This will be found to be midway between the temperatures of the hot and cold waters.

In other words, the 100 grams of hot water has fallen in temperature just as much as the 100 grams of cold water has risen in temperature. Compare this result with the case of two cylinders of equal sectional area in the hydrostatic analogy just discussed.

EXPT. 29.—Take 200 grams of water at 60° C. and pour this into a beaker containing 100 grams of cold water the temperature of which has been previously observed. Notice that the fall in temperature of the hot water is now equal to *half* the rise of temperature of the cold water.

Unit Quantity of Heat.—The above experiments lead us to conclude that two grams of water will give up twice as much heat as 1 gram when cooled through 1° C.; just as twice as much water will flow from a vessel the sectional area or which is equal to 2 sq. cm., as would flow from one, the sectional area of which is 1 sq. cm., if the surface of the water falls through 1 cm. in both cases.

Hence we define the **unit quantity of heat as that amount which must be supplied to 1 gram of water in order to raise its temperature through 1° C.** This quantity of heat is called a **Therm** or a **Gram-Calorie.**

It may be remarked that it does not necessarily follow that the amount of heat which will raise the temperature 1 gram of water from 0° C. to 1° C., will just raise the temperature of the same mass of water from (say) 60° C. to 61° C. Experiments have shown that the quantities of heat required in these two cases are slightly different. Hence the true therm is defined as that quantity of heat which will raise the temperature of 1 gram of water from 0° C. to 1° C. For ordinary purposes, however, we may consider that 100 therms are required to raise the temperature of 1 gram of water from 0° C. to 100° C.

Specific Heat.—The quantity of heat, measured in therms, which will raise the temperature of 1 gram of a substance through 1° C., is called the specific heat of that substance.

Experimental Determination of Specific Heat. Method of Mixtures.—

EXPT. 30.—Take a piece of copper possessing a mass of about 200 grams and weigh it; call its mass w_1. After having tied a piece of thin cotton round it, so as to provide a means by which it may be conveniently removed, place it in a beaker of water which is kept briskly boiling for several minutes.

Pour about 400 c.cs. of cold water into a thin-walled beaker which has been previously weighed, and weigh both together. You can find the mass w_2 of the water by subtraction. Place a thermometer in the water, and carefully note the temperature t_1° C. that it indicates. Remove the piece of copper from the boiling water and quickly drop it into the cold water, moving it about so as to keep the water in circulation, and finally read the highest temperature t_2° C. which the thermometer indicates.

Now w_2 grams of water have been heated through $(t_2 - t_1)$° C.

If 1 gram of water is heated through 1° C., one therm of heat must have been supplied to it.

$\therefore$ Since w_2 grams of water have been heated through $(t_2 - t_1)$° C., $w_2 \times (t_2 - t_1)$ therms have been supplied to it.

Let s = the specific heat of copper, *i.e.*, the number of therms of heat which 1 gram of copper will give up in cooling through 1° C.

The temperature of the copper has fallen through $(100 - t_2)$° C. during the experiment. By definition 1 gram of copper will give up $s(100 - t_2)$ therms in cooling from 100° to t_2° C.

Therefore w_1 grams of copper will give up $w_1 s(100 - t_2)$ therms under the same conditions. The heat given up by the copper has been supplied to the water. Hence

$$w_1 s(100 - t_2) = w_2(t_2 - t_1).$$
$$\therefore s = \frac{w_2(t_2 - t_1)}{w_1(100 - t_2)}.$$

Calorimeter.—The above experiment explains the general method employed in determining the specific heat of a substance. The vessel used to contain the water, the temperature of which is to be raised by the introduction of the heated substance, is called a **Calorimeter.** Glass is not a suitable substance for the construction of a calorimeter, since its specific heat is high, and a large amount of heat is thus required to raise its temperature; whilst its thermal conductivity is low, thus entailing an uncertainty as to the temperature of parts not immediately in contact with the water. Thin sheet copper is generally used for the construction of calorimeters.

Sources of Error in the above Experiment.—

1. The temperature of the boiling water may not have been exactly 100° C. (*see* Chapters VIII.).
2. A certain amount of heat will be lost by the copper during the transference from the boiling to the cold water.
3. A certain amount of hot water will be carried on the surface of the copper.
4. A certain amount of heat will be lost by radiation, or heating the surrounding air, whilst the cold water is being warmed.
5. No allowance has been made for the heat absorbed in raising the temperature of the calorimeter and the thermometer.

NOTE.—Errors due to 2 and 3 will be diminished by taking a large mass of copper, preferably in the shape of a sphere. The error due to 4 will, however, be increased by this procedure.

Besides the above sources of error, there is the possible one due to imperfections in the thermometer used. Since we are alone concerned in such experiments as these with differences of temperature, this last source of error may at present be neglected.

The way in which errors due to the above sources can be eliminated will be made clear by considering Regnault's method of determining the specific heat of a solid.

Regnault's Experiments.—Fig. 57 gives a perspective view of Regnault's apparatus.

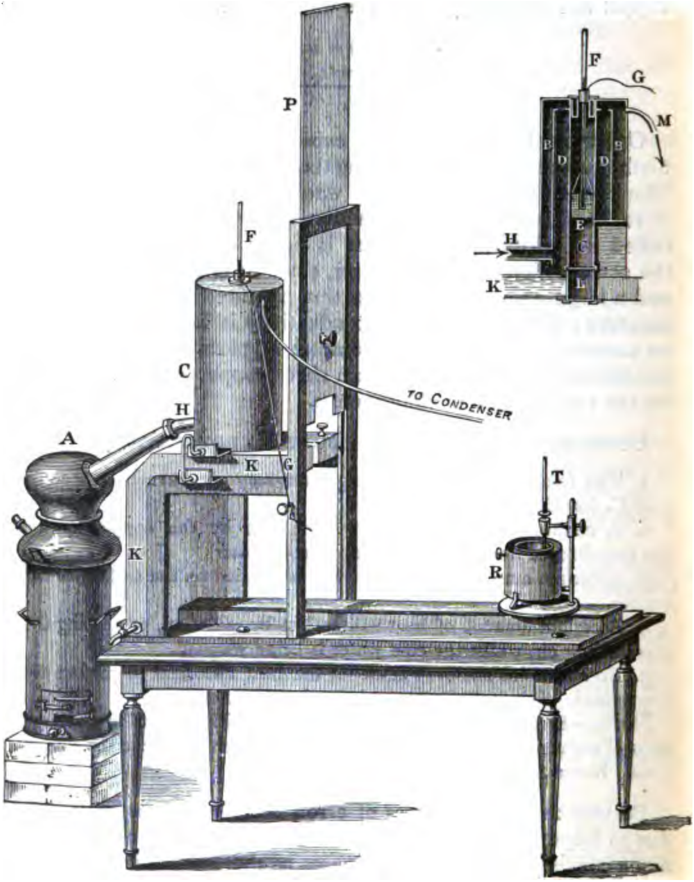

Fig. 57.—Regnault's apparatus for determining specific heats. (P.)

The substance to be experimented on was supported in a small wire cage E, the whole being heated in a vessel C surrounded by a double steam jacket DB. Thus the substance was not wetted. A considerable time (half-an-hour or more) was required for the substance to become uniformly heated throughout.

The cage was suspended in C by a fine fibre G, by means of which it could be lowered when occasion required.

The calorimeter R could be run immediately beneath the steam heater C when the wooden panel P had been lifted. To avoid the communication of heat to the calorimeter either by the boiler A or the heater C, the stand K was made hollow and filled with cold water. The lower part of the heating chamber C was closed with a double sliding shutter. When the latter was opened, the substance, (which had been heated in C to a temperature indicated by the thermometer F), was quickly lowered into the calorimeter, the latter being then removed and the panel P closed.

In order to prevent losses due to the transference of heat from the calorimeter and its contents during the interval that elapsed between the introduction of the heated substance and the completion of the experiment, the calorimeter, which was made of thin copper, was supported in another copper vessel, a narrow air space being provided between the two.

The rate of cooling of the calorimeter can also be diminished by designing it to contain a larger quantity of water. For the amount of heat lost per second, for a given difference of temperature between the water and the surrounding air, is proportional to the exposed surface, *i.e.*, to the square of the dimensions of the calorimeter. The total quantity of heat which has been communicated to the calorimeter for the same difference of temperature is, however, proportional to the volume of the water, *i.e.*, to the cube of the dimensions of the calorimeter. Hence the ratio of the heat lost per second, to the total amount of heat communicated by proportional quantities of the heated substance, will vary inversely as the linear dimensions of the calorimeter.

Elimination of Errors due to Cooling of Calorimeter. —Rumford's method.—Such error as may occur when the above precautions are taken may be further diminished by the following method due to Count Rumford. A preliminary experiment is performed in order to determine the approximate rise of temperature. In performing the final experiment, the initial temperature of the calorimeter is arranged to be approximately as much below the temperature of the surrounding air, as the final temperature will be above it. Thus during the first half of the interval occupied by the transference of heat to the calorimeter and its contents, these will be below the temperature of the air, and will therefore absorb heat from surrounding bodies.

During the second half of the interval, the calorimeter and its contents will be warmer than surrounding bodies, and will therefore communicate heat to them. With the arrangement indicated above, the heat gained in the first half will be approximately equal to that lost during the second half of the interval.

Water Equivalent of Calorimeter.—The mass of water which would require the same quantity of heat to raise its temperature through 1° C. as is required by the calorimeter for this purpose, is called the water equivalent of the calorimeter. Thus if w_0 = mass of calorimeter when empty, s_0 = specific heat of the substance of which the calorimeter is composed, the amount of heat necessary to raise the temperature of the calorimeter through 1° C. = w_0s_0 therms. This would raise w_0s_0 grms. of water through 1° C. Therefore the water equivalent of the calorimeter is equal to w_0s_0.

If this value is added to the mass of water contained in the calorimeter the error due to (5) above is avoided.

For accurate work the water equivalent of the thermometer and the stirrer must be found and added to that of the calorimeter.

To Determine the Specific Heat of a Liquid.—

EXPT. 31.—This determination may be performed in two ways, as follows:—

1. *When a mass of metal of known specific heat is provided.*—Place the liquid in the weighed calorimeter and weigh both together. Obtain the mass w_2 of the liquid by subtraction. Let w_1 be the mass, and s the known specific heat of the solid provided.

Heat the solid either in a steam jacket, when that is provided, or in boiling water, as previously described. Note the temperature t_1° C. of the liquid, and quickly transfer the heated solid to the calorimeter. Note the final temperature t_2° C. attained by the calorimeter and its contents.

Let S = specific heat of liquid.
s = known specific heat of the solid used.

The heat gained by liquid $= w_2 S\,(t_2 - t_1)$

" lost " solid $= w_1 s\,(100 - t_2)$.

$$\therefore\ w_2S(t_2 - t_1) = w_1s(100 - t_2).$$

$$S = \frac{w_1s(100 - t_2)}{w_2(t_2 - t_1)}.$$

2. *By allowing the liquid to impart heat directly to water.*—Heat a weighed quantity of the liquid, contained in a thin walled test-tube of large capacity, noting its temperature by means of a thermometer pushed through a hole in the cork closing the mouth of the tube (*see* Fig. 55).

The test-tube is then immersed, as far as the surface of the contained liquid, in a calorimeter containing a weighed quantity of water, the temperature of which is indicated by a second thermometer.

Support the test tube by means of the thermometer (*see* Fig. 55, p. 118) and shake it gently so as to keep the contained liquid, as well as the water in the calorimeter, in circulation. Note the fall in the temperature of the liquid, and the corresponding rise in the temperature of the water, after a few minutes. Equate the heat lost by the liquid to that gained by the water, and thus deduce the value of the specific heat of the liquid.

Taking the specific heat of glass as ·2, apply a correction for the heat given out by the immersed part of the glass test tube.

Method of Cooling.—

EXPT. 32.—Take a flask of about 300 c.cs. capacity, and fill it up to the neck with water at a temperature of about 60° C. Support this flask on a frame made from cardboard, in the manner indicated in Fig. 58. Stir the water continually by means of a thermometer, and take

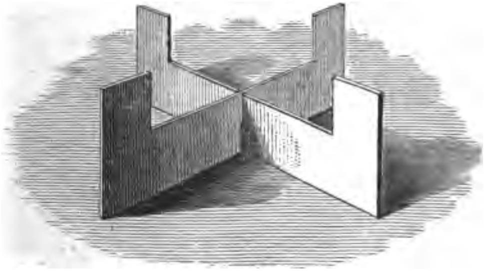

FIG. 58.—Cardboard stand for supporting a calorimeter or the flask used in Expt. 32.

readings of the temperature indicated; at first, every half minute, and later, when the cooling takes place more slowly, at longer intervals. Observe also the temperature of the surrounding air. Enter your results in a table similar to the following:—

Time.	Temperature of Water.	Temperature of surrounding Air.

Finally plot your results in a diagram similar to Fig. 59. Time is measured horizontally from O to X, whilst the corresponding thermometer readings are measured vertically parallel to OY.

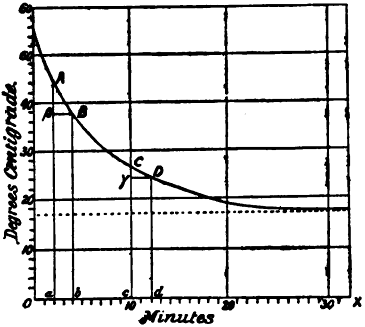

FIG. 59.—Cooling curve for water.

The connection between the rate at which the water is cooling and its mean temperature during a given interval may now be obtained. Let Aa, Bb, be two lines drawn perpendicular to OX, through points indicating a difference of two minutes of time. Draw Bβ parallel to OX; then Aβ indicates the fall of temperature in two minutes when the mean temperature of the water is equal to $\frac{\text{A}a + \text{B}b}{2}$. Since A$a$ = 44·5° C., Bb = 38° C.,

$$\text{Mean temperature during two-minute interval} = \frac{44{\cdot}5 + 38}{2} = 41{\cdot}2^\circ \text{ C.}$$

Draw a horizontal line through 17° C., which was the temperature of the room during the above experiment. Then the mean difference in temperature between the water and the room was, during the above two-minute interval, equal to 41·2 − 17 = 24·2° C. The fall in temperature Aβ = 6·5° C.

The ratio of the fall of temperature during the two-minute interval, to the mean difference in temperature between the water and the room, was therefore equal to $\frac{6{\cdot}5}{24{\cdot}2} = {\cdot}268$.

Now take two other points c, d, at a distance apart along OX indicating a two-minute interval, and draw the vertical lines Cc, Dd. Proceeding as above, we obtain the following results.

Mean temperature during this two-minute interval =

$$\frac{27 + 24{\cdot}7}{2} = 25{\cdot}8^\circ \text{ C.}$$

Mean difference of temperature between the water and the room during the interval = $25{\cdot}8 - 17 = 8{\cdot}8^\circ$ C.

Fall of temperature during this interval = $C\gamma = 2{\cdot}3^\circ$ C.

∴ Ratio of fall of temperature during this two-minute interval, to the difference of temperature between the water and the room $= \frac{2{\cdot}3}{8{\cdot}8} = {\cdot}262$, which is practically equal to the value previously obtained.

Repeat this process at various points of the curve.

The results obtained show that the rate at which the flask cools is proportional to the difference between its temperature and that of its surroundings.

Now for each fall in temperature of 1° C. a certain amount of heat has left the water. Nearly all of this heat has passed through the glass walls of the flask, having finally been directly communicated to the air, or radiated to surrounding objects. It is almost self-evident that the amount of heat leaving the exterior of the flask, during an interval in which the temperature of the glass is on an average a certain number of degrees above that of the surroundings, will be independent of the nature of the contained liquid.

Hence we arrive at the following law, which is a particular case of **Newton's Law of Cooling**:—

The amount of heat lost, in a given interval of time, by a particular vessel when filled with any liquid, is proportional to the mean difference of temperature between the vessel and the surrounding air.

We can now determine the specific heat of a liquid by observing the time occupied in cooling from one temperature to another.

Expt. 33.—A quantity of warm water is enclosed in a test-tube, the mouth of which is closed by a cork pierced to admit a thermometer T and a wire-stirrer S (*see* Fig. 60), and the whole is placed in an enclosure, such as a tin can, the walls of which are kept at a constant temperature by being surrounded by melting ice. Notice the time θ_1 that is required for the temperature to fall from a certain value, t_1, to another value, t_2, the water being kept well stirred. Now replace the water by an equal volume of the liquid of which the specific heat is required, and observe the time θ_2 occupied in cooling from t_1 to t_2, under similar conditions.

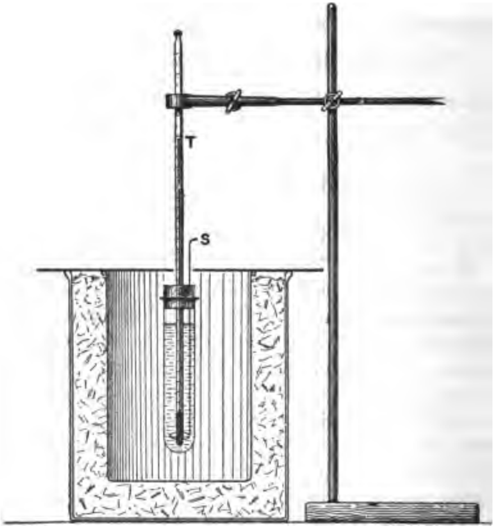

FIG. 60.—Apparatus for determining the specific heat of a liquid by the method of cooling.

The liquid and water have both possessed the same mean temperature during cooling, but different times will generally have elapsed.

In accordance with the law enunciated above, the total quantity of heat which has left the vessel will be proportional to the time taken by the liquid in cooling from t_1 to t_2. Hence, if w_1 was the mass of the water, and w_2 that of the liquid of which the specific heat s is to be determined, we have

$$\frac{\text{Heat lost by liquid}}{\text{Heat lost by water}} = \frac{w_2 s\ (t_2 - t_1)}{w_1\ (t_2 - t_1)} = \frac{\theta_2}{\theta_1}$$

$$\therefore\ s = \frac{w_1}{w_2} \cdot \frac{\theta_2}{\theta_1}\ .$$

If the experiment is conducted as previously described, a great part of the cooling is due to the direct communication of heat to the air. Consequently air currents are set up, and these may slightly vitiate the results of the experiment.

Dulong and Petit, who, as well as Regnault, tried this method, placed the cooling vessel in a chamber which was afterwards thoroughly freed from air, its walls being kept at a constant temperature by being surrounded with melting ice. In this case heat is lost only by radiation (*see* Chap. XXI).

This method gives good results for the specific heats of liquids, but is inapplicable to solids. When a solid cools, the outer layers are always at a lower temperature than the inner core. Consequently the conductivity of the solid greatly affects the time it will take to cool through a given number of degrees.

Correction for Heat lost by Radiation and Convection during Calorimetric Experiments. — The method employed for this purpose may be best understood by following a particular example.

The initial temperature of a calorimeter and its contained water was found to be 16·72° C., the surrounding air having the same temperature. The heated solid having been introduced, the temperature of the water in the calorimeter was observed at the end of each ensuing minute. These temperatures were plotted as ordinates on squared paper, the corresponding times being abscissæ. The continuous line curve in Fig. 61 was thus obtained. The rate of cooling when the solid and the water were at the same temperature was found by drawing the last two crosses on the descending part of the curve. The corresponding fall of temperature was 1° C., and had occurred in $2\frac{1}{2}$ minutes. The mean temperature during this interval was 35° C.

$\therefore$ Rate of fall of temperature, at 35° C. $= \frac{1}{2\frac{1}{2}} = \frac{2}{5} = \cdot 4°$ C. per minute.

Fig. 62 was next drawn, exhibiting the rate of fall of temperature, for any mean temperature. ·4° was plotted vertically

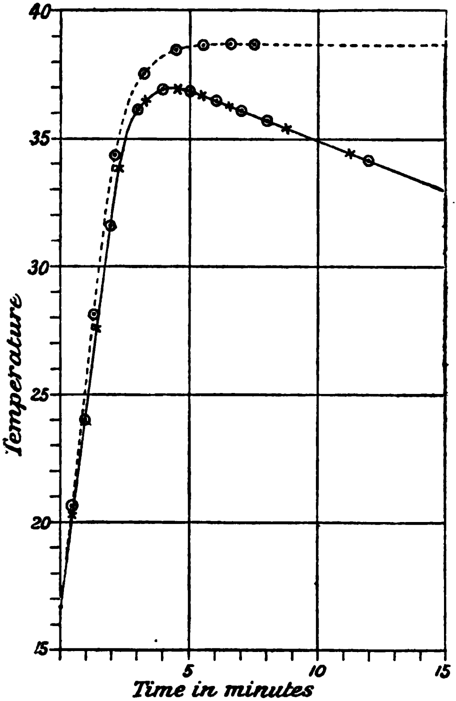

FIG. 61.—Method of determining the loss of heat from calorimeter during heating.

above 35°, and the point so obtained was joined by a straight line to 16·72°, the temperature of the room, at which the rate of cooling would be zero.

In order to obtain a curve representing the temperature changes which would have occurred had no heat been lost by radiation, &c., the following table was constructed :—

Interval.	Initial temp.	Final temp.	Mean temp.	Cooling during minute (from Fig. 62.)	Correction to be added to mean temp.	Mean temp. during each minute + correction.
1st minute	16·72°	24°	20·36	·08	·08	20·44
2nd ,,	24°	31·5°	27·75	·24	·08 + ·24 = ·32	28·07
3rd ,,	31·5	36·2	33·85	·37	·32 + ·37 = ·69	34·54
4th ,,	36·2	37·0	36·60	·44	·69 + ·44 = 1·13	37·73
5th ,,	37·0	37·0	37·00	·45	1·13 + ·45 = 1·58	38·58
6th ,,	37·0	36·5	36·75	·44	1·58 + ·44 = 2·02	38·79
7th ,,	36·5	36·1	36·30	·43	2·02 + ·43 = 2·45	38·75
8th ,,	36·1	35·7	35·9	·42	2·45 + ·42 = 2·87	38·77
&c.						

The method employed was as follows :—

From Fig. 61 it is seen that at the beginning and end of the first minute the temperatures were 16·72° and 24° C. respectively. Hence, mean temperature during first minute $= \frac{16{\cdot}72 + 24}{2} = 20{\cdot}36$. Referring to Fig. 62, it can be seen that at the mean temperature 20·36° C., the temperature is falling at the rate of ·08° C. per minute. Hence, if no cooling had taken place. the mean temperature during the first minute would have been 20·36 + ·08 = 20·44° C.

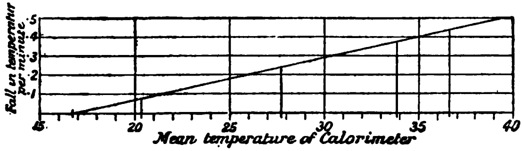

Fig. 62.—Rate of cooling of calorimeter, for various temperatures.

In a similar manner the cooling during the second minute was determined. This was added to the cooling during the first minute (*see* column 6) to obtain the correction to be added to the mean temperature during the second minute.

Proceeding in this way, the last column of the table was finally obtained. The figures in this column represent the mean temperatures that would have obtained during successive minutes had no cooling occurred. It is seen that after the fifth minute the values become practically constant; they would have been still more nearly constant if Figs. 61 and 62 had been drawn on a larger scale. The points representing the mean observed temperature during each minute were then marked with crosses on the observation curve, and the corrected mean temperatures were marked off vertically over these points.

The points so obtained were then joined by the dotted curve, which represents the rise in temperature which would have occurred had no heat been lost by radiation, &c.

Specific Heat of Ice.—This was determined by Person in the following manner. A thin copper vessel, provided with a thermometer projecting into its interior, was partially filled with water and then placed in a freezing mixture. The water was frozen, and reduced to a temperature considerably below 0° C.

The vessel with its contained ice was then removed and placed in a calorimeter containing warm water, kept well stirred. The temperature of the water at once began to fall, whilst the temperature of the ice rose.

If the temperature of the warm water, the mass of which was w_1, fell through $t_1°$ in a certain interval, then $w_1 t_1°$ therms were given up.

Assuming this heat to have passed into the ice (none of which is supposed to have melted), raising its temperature through $t_2°$; then if w_2 = mass of ice, and s = its specific heat, we have

Heat gained by ice ($= s w_2 t_2$) = heat lost by water ($= w_1 t_1$.)

$$\therefore s w_2 t_2 = w_1 t_1.$$

$$\therefore s = \frac{w_1 t_1}{w_2 t_2}.$$

By this means Person found the specific heat of ice to be equal to ·504.

Specific Heat of Water.—The fact that the quantity of heat which would raise the temperature of 1 gram of water from 0° C. to 1° C. is not exactly equal to that required to raise the temperature of the same mass of water from (say) 60° to 61° C., was first proved by Rowland in connection with his determination of the mechanical equivalent of heat. He found that the quantity of heat necessary to raise the temperature of 1 gram of water through 1° C., decreased as the temperature rose from

0° to 30°, and then increased as higher temperatures were reached. Fig. 63 shows the variations in the specific heat of water, according to Bartoli and Straciati, taking the unit of heat as that quantity which would raise the temperature of 1 gram of water, initially at 0° C., through 1° C.

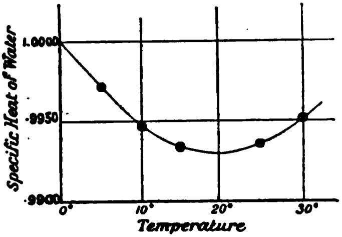

Fig. 63.—Curve showing the specific heat of water at various temperatures (sp. ht. at 0° = 1).

The values given must be understood to have the following meaning. Let a gram of water be heated from $\left(t-\frac{dt}{2}\right)$° C. to $\left(t+\frac{dt}{2}\right)$°C. where dt is a *small fraction* of a centigrade degree, and let dq represent the quantity of heat absorbed in this operation. Then the specific heat of water at t° C. $= \frac{dq}{dt}$.

According to Fig. 63, the specific heat of water has a minimum value at 20° C.

The following table, due to Callendar and Barnes (B. A. report, 1899), gives the specific heat of water for temperatures between 0° and 100°C. The unit of heat chosen is that quantity which is required to raise the temperature of 1 gram of water through 1°C. in the immediate neighbourhood of 20°C. At 20°C. the specific heat of water acquires its mean value between 0° and 100°. It has a minimum value at 40°.

Temp. C.	Sp. Ht.	Temp. C.	Sp. Ht.	Temp. C.	Sp. Ht.	Temp. C.	Sp. Ht.
0	1·0054	20	1·0000	40	·9982	60	1·0000
5	1·0037	25	·9992	45	·9983	75	1·0024
10	1·0022	30	·9987	50	·9987	90	1·0053
15	1·0010	35	·9983	55	·9992	100	1·0074

Although the use of water as a calorimetric substance has been almost universal up to within very recent times, several considerations lead to the conclusion that such an use is not altogether justifiable. In the first place, the relatively high specific heat of water renders it impossible to obtain variations in its temperature which can be accurately measured, without supplying large quantities of heat; whilst the variation of the specific heat of water renders its use extremely objectionable for very accurate work.

It has recently been proposed by Mr. Griffiths that liquid aniline should be used as a calorimetric substance. It appears to possess neither of the disadvantages mentioned above. On the other hand, it is a hygroscopic substance, and the presence of water may alter its specific heat by about two per cent. For this reason Bartoli recommends the use of one of the higher paraffins.

Variations in the Specific Heat of a Substance.—The specific heat of a substance generally varies with the state of the substance.

1. **Change of State.**—The specific heat of a solid is not usually equal to that of the same substance in a liquid or gaseous condition. As a general rule, the specific heat of a substance is greatest in the liquid state.

SPECIFIC HEATS OF SUBSTANCES.

Substance.	State.		
	Solid.	Liquid.	Gaseous.
Water	0·504	1·000	0·477
Mercury	0·0319	0·0333	—
Bismuth	0·0298	0·0363	—
Lead	0·0315	0·0402	—
Bromine	0·084	0·107	0·055

As a general rule fusion produces only a small change in the specific heat of a metal. This change is generally greatest in the case of metals of which the volumes are changed considerably by melting.

2. **Change from Crystalline to Amorphous Condition.**—The specific heat of an elementary substance, which can exist either in an amorphous or crystalline condition, is as a rule dependent on the condition which it happens to be in.

Thus, according to Regnault, the mean specific heat of carbon, between 8° C. and 98° C., may have any of the following values according to its condition.

Wood Charcoal.	Gas Coal.	Native Graphite.	Furnace Graphite.	Diamond.
0·2415	0·2036	0·2017	0·1970	0·1469

The specific heat of crystallised arsenic is 0·083, whilst amorphous arsenic has a specific heat of 0·076. Yellow phosphorus has a specific heat of 0·202, whilst the red variety of the same substance has a specific heat of 0·169.

3. **Presence of Impurities.**—The presence of impurities may greatly alter the specific heat of a substance. Perhaps the most remarkable change produced by mixing two substances is afforded by the case of aqueous solutions of alcohol. The specific heat of pure ethyl alcohol between 16° and 30° C. is 0·6019. On the other hand, a ten per cent. solution of alcohol in water has a specific heat of 1·032 between the same temperatures, whilst the specific heat of a 20 per cent. solution is equal to 1·046. This solution possesses a higher specific heat than any other liquid at a temperature less than 100° C.

The addition of more alcohol diminishes the specific heat of the mixture, which reaches a value of 1·026 for a 30 per cent. solution, and 0·981 for a 40 per cent. solution.

4. **Variation of Specific Heat with Temperature.**—The quantity of heat required to raise the temperature of a gram of a substance through 1° C. increases, as a general rule, with the initial temperature of the substance.

Thus, according to Weber, diamond has a specific heat of ·095 at 0° C., ·19 at 100° C., and ·459 at 985° C.

Silicon shows a similar increase of specific heat with temperature.

Alcohol possesses a specific heat of ·602 between 16° and 30° C., which value is increased to 1·114 at 160° C.

Atomic Heats.—Dulong and Petit's Law.—If masses of the various elements, numerically equal to their respective atomic weights, be taken, it is plain that equal numbers of atoms will be comprised in all cases. Thus, since the ratio of the weight of an atom of aluminium to that of an atom of lead is equal to $\frac{27·04}{206·39}$, it follows that 27·04 grams of aluminium will comprise the same number of atoms as exist in 206·39 grams of lead. Since the specific heat is equal to the number of therms which will raise the temperature of 1 gram of the substance through 1° C., if we multiply the specific heats of the various elements by the corresponding atomic weights, we obtain the quantities of heat which will raise the temperature of masses of the various elements, comprising equal numbers of atoms, through 1° C.

The following table gives the atomic weights and the specific heats of the best known of the elements ordinarily existing in a solid condition, together with the products of these quantities, constituting the *atomic heat* of those elements.

ATOMIC HEATS OF ELEMENTS IN THE SOLID STATE.

Element.	Atomic Weight.	Specific Heat.	Atomic Heat.
Aluminium	27·04	0·2022	5·45
Antimony	119·60	0·05073	6·05
Arsenic	74·90	0·0814	6·10
Barium	136·86	0·047 (?)	6·42
Bismuth	207·5	0·0298	6·17
Boron	10·9	0·252 at 30° 0·5 at 600°	2·33 5·45
Bromine (solid)	79·76	0·0843	6·70
Cadmium	111·7	0·0548	6·11
Calcium	39·9	0·180	7·20
Carbon	11·97	·238 at about 30° ·458 at 980°	2·85 5·47
Cerium	141·2	0·0448	6·31
Chromium	52·45	0·0997	5·23
Cobalt [1]	58·55	0·10303	6·03
Copper [1]	63·18	0·09232	5·82
Gold [1]	195·74	0·03035	5·94
Iodine	126·54	0·0541	6·34
Iridium	192·5	0·0303	5·83
Iron [1]	55·88	0·10983	6·13
Lead	206·39	0·0315	6·50
Lithium	7·01	·9408	6·61
Magnesium	23·94	0·245	5·86
Manganese	54·8	0·122	6·68
Mercury	199·8	0·0319 (solid)	6·36
Molybdenum	95·9	0·0659	6·31
Nickel [1]	58·24	0·10842	6·31
Palladium	106·20	0·0592	6·30
Phosphorus (yellow)	30·96	0·202	6·31
Platinum [1]	194·3	0·03147	6·09
Potassium	39·03	0·165	6·45
Rhodium	104·10	0·058	6·05
Silicon	28·0	0·1596 (at 10°C.) 0·2029 (at 232°C.)	4·39 5·68
Silver	107·66	0·0559	6·10
Sodium	22·99	0·2934	6·74
Strontium	87·3	0·074 (?)	6·45
Sulphur	31·98	0·1844	6·02
Tellurium	127·7 (?)	0·0475	6·06
Thallium	203·7	0·03355	6·81
Tin	117·35	0·0559	6·65
Tungsten	183·6	0·035	6·43
Uranium	239·8	0·028	6·71
Zinc	64·88	0·0935	6·05

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[1] The specific heats of these metals are taken from Prof. Tilden's paper, *Phil. Trans.*, June, 1900, pp. 233–255.

A glance at this table is sufficient to show that the atomic heats of the elements are approximately constant as long as the elements remain in the solid condition. Thus, taking lithium as the element with the smallest atomic weight (7·01), and uranium as the element with the highest atomic weight (239·8), we find that the products of these atomic weights into the corresponding specific heats are equal to 6·61 and 6·71 respectively; numbers which, though not exactly equal, are sufficiently nearly so to render it very unlikely that the agreement should be accidental. Hence we may conclude that *Dulong and Petit's Law*, that "**the product of the specific heat by the atomic weight is the same for all the elementary substances,**" is very approximately true for elements existing at ordinary temperatures in the solid state.

With a view to determine whether the variations generally found in the atomic heats of the elements are due to impurities, Prof. Tilden has recently determined the specific heats of a number of metals which had been carefully purified. He found that the atomic heats of the pure metals were not exactly equal. (See table, p. 138.) He concludes that in the neighbourhood of – 273° C. (the absolute zero) the atomic heat for both nickel and cobalt would be 4·0.

The variations in the atomic heats of the elements are not to be wondered at, when we remember that the specific heat of a substance varies with the temperature. Thus the atomic heats of boron, carbon, and silicon are abnormal at ordinary temperatures, but approximately attain the normal value at high temperatures.

Bromine and mercury are liquid at ordinary temperatures. Their atomic heats may be found in the following table:—

Element.	Atomic Weight.	Specific Heat.	Atomic Heat.
Bromine	69·9	0·0802	5·61
Mercury	199·8	·0333	6·64

The atomic heats of the elementary gases are seen, from the following table, to agree fairly amongst themselves, although possessing a different common value from that pertaining to solids.

Element.	Atomic Weight.	Specific Heat.	Atomic Heat.
Chlorine	35·37	0·1155	3·94
Hydrogen	1	3·409	3·409
Nitrogen	14·01	·2438	3·41
Oxygen	15·96	·2175	3·47

It will be seen, when we come to consider the kinetic theory of gases, that a very simple explanation may be given of the approximate agreement between the atomic heats of the elements existing in the same state.

Molecular Heats.—Attempts have been made to extend Dulong and Petit's Law to compound bodies. According to Woestyn, the atoms in a compound preserve their original thermal capacities, *i.e.* it requires as much heat to raise the temperature of the lead combined with a due amount of oxygen to form lead oxide, as if the lead were free.

In order to see how far this generalisation may be trusted, let us calculate the specific heat of ethyl alcohol (C_2H_6O).

Heat required to raise the temperature of 2 × 11·97 grms. of carbon by 1° C. = 2 × 5·47 = 10·94 therms.

Heat required to raise the temperature of 6 × 1 grms. of hydrogen by 1° C. = 6 × 3·409 = 20·454 therms.

Heat required to raise the temperature of 1 × 15·96 grms. of oxygen by 1° C. = 3·47 therms.

∴ According to Woestyn's hypothesis, heat required to raise the temperature of (23·94 + 6 + 15·96) = 45·90 grms. of alcohol through 1° C. = 34·864 therms.

$$\therefore \text{Specific heat of alcohol} = \frac{34{\cdot}864}{45{\cdot}9} = {\cdot}76.$$

The value experimentally obtained for the specific heat of alcohol varies between ·547 at 0° to ·859 at 120°, thus showing a general agreement.

The specific heat of carbon bisulphide varies much less with the temperature than alcohol. We will therefore see how far the calculated value of the specific heat of CS_2 agrees with the value determined from experiment.

Heat required to raise 11·97 grms. of carbon through 1°C. = 5·47 therms
,, ,, ,, 2 × 31·98 = 63·96 grms. of sulphur through 1° C. = 12·04 therms

∴ Heat required to raise 75·93 grms. of CS_2 through 1° C. = 17·51 therms

$$\therefore \text{ Specific heat of } CS_2 = \frac{17{\cdot}51}{75{\cdot}93} = {\cdot}23 \text{ therms per degree C.}$$

The value experimentally determined for the specific heat of CS_2 varies between ·235 at 0° and ·240 at 30° C.

Regnault has verified Woestyn's hypothesis in the case of alloys, the temperatures of which were far removed from the fusing point.

An interesting application of Woestyn's theory has been made in determining the specific heat of water combined with salts to form hydrates. It has been found, both from theory and experiment, to be equal to that of ice, thus leading to the conclusion that water combined with hydrates exists in the solid form.

SUMMARY.

Quantity of Heat.—In order to account for the fact, that when a hot body is placed in contact with a cold one, the temperature of the hot body falls, while that of the cold one rises, it is assumed that something, which we term *Heat*, passes from the hot to the cold body. In a similar manner water will flow from a vessel in which the surface is high to another in which the surface is lower. Difference of temperature corresponds to difference in the level of the surfaces, and quantity of heat to quantity of water transferred.

Unit Quantity of Heat is absorbed (or given up) by one gram of water when its temperature is raised (or lowered) through 1° C. This quantity of heat is called a *therm*. For accurate work, the initial temperature of the water must be 0° C.

A calorie is equal to 1,000 therms. This quantity of heat would raise the temperature of a kilogram of water through 1° C. The term *gram-calorie* is sometimes used as equivalent to therm.

Specific Heat.—The quantity of heat, measured in therms, which will raise the temperature of one gram of a substance through 1° C., is called the specific heat of that substance.

Methods of Determining Specific Heat.—

(1) *Method of Mixtures.*—A body of known mass and temperature is allowed to impart heat to water, or some other liquid of known specific heat, and the consequent rise in temperature of the liquid is observed. The heat lost by the body is then equated to that gained by the liquid.

(2) *Method of Cooling.*—The time required for approximately equal volumes of two liquids to cool through the same range of temperature, when placed in the same vessel, is observed. The heat lost in either case is proportional to the time occupied in cooling.

A Calorimeter is an instrument used for measuring quantities of heat. The water equivalent of a calorimeter is equal to the mass of water that would require, in order to raise its temperature through 1° C., an amount of heat equal to that required by the calorimeter in the same circumstances.

The Specific Heat of Ice at 0° C. is equal to 0·504 therms per 1° C. It is thus equal to about one-half of the specific heat of water at 0° C.

The Specific Heat of Water varies from 1 at 0° C. to 1·03 at 100° C., and has a minimum value somewhere between 20° C. and 30° C.

Variations in Specific Heat.—The specific heat of a substance is changed—

(1) by change of state;
(2) by presence of impurities;
(3) by a change of temperature.

Atomic Heats.—Masses of elementary substances equal to the atomic weights of the respective elements will comprise equal numbers of atoms. The atomic heats of substances are obtained by multiplying the specific heats by the atomic weights of the substances.

Dulong and Petit's Law states that the atomic heats of elementary substances in the same state are equal. Boron, silicon, and carbon possess abnormal atomic heats at low temperatures, but ordinary atomic heats at high temperatures.

The Specific Heat of a Chemical Compound can be approximately calculated from the atomic heats of its elementary constituents (Woestyn's hypothesis.)

QUESTIONS ON CHAPTER VI.

(1) Explain a method of determining the specific heat of a metal, stating what apparatus is required and what precautions are necessary for an accurate determination.

(2) Write a short essay on the relation between the specific heat of a compound body and its chemical composition.

(3) Write a short essay on the specific heats of mixtures and compounds.

(4) In measuring the specific heat of a substance by the method of mixtures, the rise in temperature of the water in the calorimeter has to be determined. Show how the observations are corrected for the loss of heat by radiation during the time the temperature is rising.

(5) Write a short essay on the change in the specific heat of water with temperature.

(6) When 120 grams of a given liquid, enclosed in a copper vessel whose mass is 20 grams, are heated to 100° C. and immersed in 300 grams of water at 13 °C. contained in a copper calorimeter whose mass is 80 grams, the temperature rises to 27·5° C. Assuming the specific heat of copper to be 0·1, find that of the liquid.

(7) Discuss the relation between the specific heats and the atomic weights of bodies.

(8) Describe a mode of determining the specific heat of a solid. A mass of 700 grams of copper at 98° C., put into 800 grams of water at 15° C., contained in a copper vessel weighing 200 grams, raises the temperature of the water to 21° C. Find the specific heat of the copper.

(9) What is meant by the specific heat of a substance? What methods would you employ to determine the specific heat (1) of a solid, (2) of a liquid?

(10) A piece of ice at 0° C., weighing 12 grams, is put into a vessel with water equivalent 20, and containing 180 grams of paraffin oil at 20° C. When the ice is all melted the temperature of the mixture is 10° C. Taking the latent heat of water as 80, find the specific heat of the paraffin oil.

(11) Describe the specific heat of a substance, and explain some one way of measuring it. 154 grams of a certain substance at 212° F. are placed in a vessel containing 182 grams of water at 15° C., and both come to a final temperature of 24° C., calculate the specific heat of the body, and explain why the number determined is the specific heat as defined.

(12) Define the unit quantity of heat, and calculate how many units of heat were given out by a body which, when placed in a calorimeter, raised its temperature from 15° C. to 38° C., there having been 375 grams of water in the calorimeter, which weighed 104 grams, and was made of a metal whose specific heat was 0·43.

(13) Describe an experiment to show that the quantity of heat required to raise the temperature of one pound of water through any degree between 0° C. and 100° C. is very nearly the same. To what sources of error is your experiment liable?

(14) A copper vessel contains 100 grams of water at 12° C. When 56 grams of water at 30° C. are added, the resulting temperature of the mixture is 18° C. What is the water equivalent of the calorimeter?

A calorimeter with water equivalent 12 contains 100 grams of water at 12° C. When 100 grams of a metal at 100° C. are added, the resulting temperature of the mixture is 20° C. Find the specific heat of the metal.

PRACTICAL.

(1) Find the specific heat of the given metal.

(2) Find by the method of cooling the specific heat of the given liquid.

(3) Find the amount of heat developed when water and sulphuric acid are mixed in the proportion of 10 to 1 by volume.

(4) Find the specific heat of ice, given paraffin oil of specific heat 0·5 and a freezing mixture.

(5) Determine the specific heat of a given body by method of mixture.

(6) Measure the specific heat of a given solid, applying corrections for the materials of the calorimeter, &c.

(7) Compare the specific heat of the given liquid with that of the given solid.

(8) Find the amount of heat evolved per c.c. of the mixture, when sulphuric acid and water are mixed in the proportion of 1 to 10 by volume.

CHAPTER VII

LATENT HEAT OF FUSION AND VAPORISATION

WHEN heat is communicated to a substance, a rise of temperature may not be the only result produced. Indeed, it is possible, in certain circumstances, to communicate a considerable quantity of heat to a substance without producing any alteration in temperature. In such cases the heat supplied is utilised in changing the state of the substance.

EXPT. 34.—Take a weighed calorimeter and half fill it with water, at a temperature of about 30° C. Weigh the calorimeter and its contents, and obtain the mass of the water by subtraction.

Take a piece of ice, possessing a mass about ⅙th of that of the water in the calorimeter. Wrap this ice in a piece of dry flannel. By this means any moisture on the surface of the ice will be removed, whilst the formation of more moisture by the melting of the ice will be prevented, the flannel being a bad conductor of heat.

Place a thermometer in the water contained in the calorimeter, and note the temperature which it indicates. Remove the ice from its flannel wrappings, and quickly drop it into the water in the calorimeter. Stir by means of the thermometer, and note the temperature indicated when the ice has just melted.

Remove the thermometer, and again weigh the calorimeter and its contents. Find by subtraction the mass of ice which has been melted.

Now the heat yielded up by the warm water in cooling from its initial to its final temperature may be directly calculated from the mass and fall in temperature of the water. Similarly, the heat absorbed in raising the temperature of the water derived from the ice, from 0° C. (the temperature of melting ice) to the final temperature of the water in the calorimeter, may be calculated.

It will be found that the first mentioned quantity of heat is greatly in excess of the latter quantity. Hence a certain quantity of heat has been absorbed, or rendered latent, during the change from the solid to the liquid state.

The Latent Heat of Fusion of a substance is the quantity of heat required to convert one gram of the substance from the solid to the liquid state, no change meanwhile occurring in its temperature.

A formula for obtaining the latent heat of fusion of ice from the results of the foregoing experiment may now be easily derived.

Let w_1 = mass of warm water, initially at a temperature t_1° C.
Let w_2 = mass of ice added.
,, t_2 = temperature (° C.) of the contents of the calorimeter when the ice has just melted.
,, L = latent heat of fusion of ice.

Then during the cooling of w_1 grams of water from t_1° C. to t_2° C., a quantity of heat, equal to $w_1(t_1 - t_2)$ therms, has been given up.

This heat has been utilised :

1. In converting w_2 grams of ice, at 0° C., into w_2 grams of water at the same temperature. The quantity of heat thus used is Lw_2.

2. In heating w_2 grams of water from 0° C. to t_2° C. The quantity of heat necessary for this purpose is $w_2(t_2 - 0)$.

$$\therefore Lw_2 + w_2t_2 = w_1(t_1 - t_2).$$

In order to take account of the heat rendered up by the calorimeter, it is sufficient to notice that the thermal capacity, or water equivalent, of the calorimeter is equal to w_3s, where w_3 is the mass of the calorimeter, and s is the specific heat of the substance of which it is composed (p. 126). Hence the correct equation will stand as

$$Lw_2 + w_2t_2 = (w_1 + w_3s)(t_1 - t_2).$$

$$\therefore L = \frac{(w_1 + w_3s)(t_1 - t_2)}{w_2} - t_2.$$

Calculate the value of the latent heat of fusion of ice from the results of the foregoing experiment.

The correct value of L for ice is 80 therms per gram.

The foregoing experiment will render it clear that before the latent heat of fusion of a substance can be determined some other constants of the substance must be obtained. Thus, if we know the melting point of paraffin wax, together with its specific heat, both when in the liquid and the solid state, we might pour some melted paraffin wax, which had been heated to about 70° C., into a beaker containing cold water, stirring the whole, and noting the final temperature arrived at.

Then the heat given up by the wax is as follows :—

1. Heat given up while the temperature falls from 70° C. to the melting point.
2. Heat given up as the liquid wax becomes solid, the temperature remaining constant.
3. Heat given up as the solid wax cools from its melting point to the final temperature.

EXPT. 35.—*To determine the melting point of wax.*—This may be determined by dipping the bulb of a thermometer into some melted wax, the temperature of which is some degrees above the melting point. When the film of solid wax at first formed has become liquefied, remove the thermometer, and rotating it quickly in the hand, notice the temperature indicated when a film of the opaque wax makes its appearance on the outside of the bulb. Then place the bulb in some water, slowly heat this, and notice the temperature when the film disappears. The mean of these two temperatures may be taken as the melting point of the wax.

EXPT. 36.—*To determine the specific heat of liquid paraffin wax.*—Take a large beaker, or, better still, a large copper calorimeter, half filled with water at a temperature one or two degrees above the melting point of the wax. Determine the mass and temperature of this water. Take a large test tube containing a known mass of melted paraffin wax at a temperature of about 80° C, and immerse this in the water, stirring both the wax and the water, and noting the common temperature which both finally attain. The specific heat of the melted wax may be calculated in a manner similar to that previously described.

EXPT. 37.—*To determine the specific heat of solid paraffin wax.*—Cut up some solid paraffin wax into shavings, weigh them, and leave them for about a quarter of an hour in a beaker with the bulb of a thermometer placed in their midst. After taking their temperature in this manner, shoot the shavings into a beaker half full of water at about 45° C., and stir so as to be sure, as far as possible, that the wax and water attain the same final temperature. Note this common temperature. The calculation of the specific heat of the wax may now be performed.

This stage of the experiment is one of considerable difficulty, since the wax is a very bad conductor of heat, and also floats on the water.

With sufficient care, however, a tolerably accurate result may be obtained.

You may now obtain the latent heat of the wax, either by the method already sketched out, or by placing solid wax at a known temperature in a known mass of melted wax at about 80°, carefully noting the initial temperature of the latter, and the final temperature attained by the mixture.

Determination of Specific Heat by Black's Ice Calorimeter.

EXPT. 38.—Take a block of ice, of dimensions about 4" × 4" × 3", and cut an approximately hemispherical hollow through its upper surface (Fig. 64). The surface of another block of ice is smoothed so as to form a cover for this arrangement. A piece of metal is heated to 100° C., either by placing it directly in boiling water, or, better, in a steam jacket (*see* Chapter VI., p. 124). When this is ready, dry out the cavity in the ice with a towel and quickly transfer the metal to it, immediately afterwards placing the ice cover in position. After about five minutes the metal will have attained the temperature of the ice, a certain amount of the latter having been converted into water at 0° C. by the heat given up during the process.

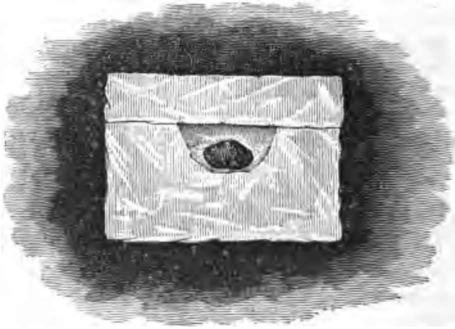

FIG. 64.—Black's ice calorimeter.

Pour this water into a weighed evaporating basin, drying the cavity by means of some weighed filter paper, and determine the mass of the ice which has been melted, by weighing and subtraction.

Let w_1 = mass of metal used.

Let s = specific heat of the metal.

Let w_0 = mass of ice which has been melted.

Thus, whilst the temperature of the metal was sinking from 100° to 0° C., $s \times w_1 \times 100$ therms were given up.

In transforming w_2 grams of ice at 0° C. into water at the same temperature, Lw_2 units of heat were absorbed, where L, the latent heat of fusion of ice, = 80.

$$\therefore\ 100\, sw_1 = Lw_2 = 80w_2.$$

$$s = \frac{w_2}{w_1} \times \frac{80}{100} = \frac{4}{5}\frac{w_2}{w_1}.$$

It may be noticed that no thermometer is required in this experiment, provided that we may assume the heated metal to be at 100° C. (or, more accurately, at the boiling point of water corresponding to the atmospheric pressure at the time of the experiment).

Lavoisier's and Laplace's Ice Calorimeter.—This piece of apparatus is shown in Fig. 65. The heated solid is placed in a metal enclosure, which is entirely surrounded by a chamber packed with broken ice. The heat communicated from the solid melts some of this ice, and the water formed runs off by the lower tap. In order to prevent this ice from being melted by heat received from surrounding bodies, an external chamber, also packed with ice, is provided, from which water can run away by the side tap. When the apparatus has stood for some time before the solid is introduced, water will cease to flow from the lower tap—a steady drip from the side tap being due to the melting of the ice in the guard chamber. The heated solid is then placed in the inner compartment, and the water which now flows from the lower tap is collected. The calculation to be performed is similar to that described in connection with Black's Ice Calorimeter.

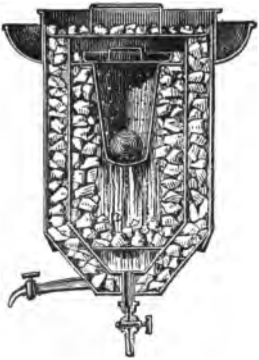

FIG. 65.—Lavoisier's and Laplace's ice calorimeter.

Lavoisier's and Laplace's calorimeter presents little except historical interest. It is almost impossible to obtain accurate results with it, since the water produced by the melting of the ice does not flow away freely, but becomes entangled amongst the remaining ice.

Latent Heat of Steam.—At a pressure of 760 mm. of mercury, and a temperature of 100° C., water and steam can exist in the same vessel. In order, however, to convert water into steam at the same temperature, a considerable quantity of heat must be supplied. As the addition of this heat does not produce any change of temperature it is said to become latent. If the temperature of the vessel is reduced, some of the steam will be condensed and will give up the heat previously rendered latent, thus tending to maintain the vessel at its initial temperature of 100° C.

The Latent Heat of Steam is defined as the quantity of heat absorbed in transforming one gram of water at its boiling point, into steam at the same temperature.

EXPT. 39.—*To determine the latent heat of steam.*—A boiler, which may be conveniently made from a clean oil-can, provided with a sound cork and a wide glass delivery tube (Fig. 66), is mounted on a tripod stand, and after being about half filled with water, is heated by means of a Bunsen burner. The glass delivery tube is connected to one end of a piece of ordinary indiarubber tubing; the latter is prevented from losing

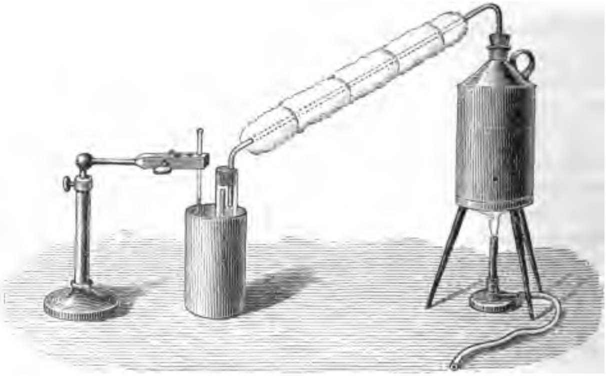

FIG. 66.—Arrangement for determining the latent heat of steam.

heat by a binding of cotton wool. At the other end of the indiarubber tube is a water trap, shown in section in Fig. 67. This is made from a piece of glass tubing of about ¾″ internal diameter, its ends being provided with corks bored to receive the glass tubes B and C. The tube B projects only a short distance beyond the lower surface of the cork, whilst the end of the tube C reaches above the lower orifice of the tube B. Thus any water, which has been formed by the condensation of steam in the indiarubber tube, will be collected, so that only dry steam issues from the tube C.

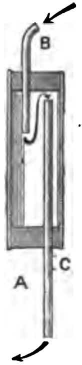

FIG. 67. Water trap.

A calorimeter is about half filled with cold water, and the mass of the calorimeter and its contents determined. It is best initially to cool this water as far below the temperature of the room as it is intended finally to heat it above that temperature. The final temperature of the water in the calorimeter should not be higher than about 30° C., in order to avoid loss of heat through the vaporisation of the water. Note the initial temperature of the water.

The lower orifice of the tube C is placed beneath the surface of the cold water in the calorimeter; the steam which condenses in the water raises the temperature of the latter. The water should be kept well stirred during the above operation. Finally, the calorimeter and its contents are again weighed, in order to determine the mass of steam which has been condensed.

Let w_1 = the mass of the water (or more accurately, the water equivalent of the calorimeter and its contents) at the initial temperature t_1° C.

Let t_2° C. = the final temperature of the calorimeter and its contents.

Let w_2 = the mass of steam condensed, determined by subtracting the initial from the final mass of the calorimeter and its contents.

Let L = the latent heat of steam.

Then the heat given up during the conversion of w_2 grams of steam at 100° C. into water at the same temperature = Lw_2.

Heat given up whilst w_2 grams of water are cooling from 100° to t_2° C. = $w_2(100-t_2)$.

Heat necessary to raise w_1 grams of water from t_1° to t_2° C. = $w_1(t_2-t_1)$.

$$\therefore Lw_2 + w_2(100 - t_2) = w_1(t_2 - t_1)$$

$$\therefore L = \frac{w_1(t_2-t_1)}{w_2} - (100 - t_2).$$

Berthelot's Apparatus for determining the Latent Heat of Steam.—In order to avoid the possibility of partial condensation taking place before the steam enters the calorimeter, Berthelot used the arrangement shown in Fig. 68. The water or other liquid, of which the latent heat is required, is boiled in a glass flask heated by means of a ring burner, *l*,

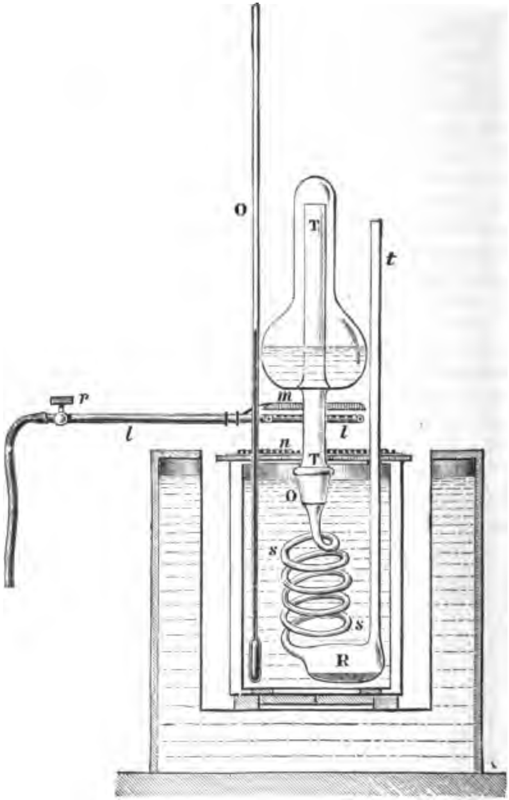

FIG. 68.—Berthelot's apparatus for determining the latent heat of steam.

placed beneath it. The vapour formed is carried down through the heated liquid by way of a vertical tube T, the upper orifice of which is above the surface of the liquid. After leaving the flask the vapour traverses a spiral tube *s* immersed in water in the calorimeter. The liquid condensed in the tube *s* is collected in the enlargement R, which communicates with the atmosphere by means of the tube *t*. The calorimeter is protected from the reception of heat from external bodies by means of a water-jacket, whilst the direct communication of heat from the ring burner is prevented by a slab of wood *n* covered with wire gauze.

The calculations to be performed, in order to determine the latent heat of the liquid from the amount of the latter condensed in the enlargement R, and the rise in temperature of the calorimeter and its contents, are similar to those already given.

Berthelot's determination resulted in a value for the latent heat of steam equal to 536·2 therms per gram.

Regnault's Experiments.—In performing the experiments about to be described, Regnault's object was not alone to determine the quantity of heat necessary to convert 1 gram of water at 100° C. into steam at the same temperature, but also to determine the heat that must be communicated to a gram of water, initially at 0° C., in order to convert this into steam at some higher temperature $t°$.

Total Heat of Steam.—The total heat of steam at $t°$ C., is defined as **the quantity of heat which must be communicated to 1 gram of water, initially at 0° C., in order to convert it into saturated vapour at a temperature of $t°$ C.**

In order to vary the boiling point of the water the pressure must be suitably modified.

Previous to the performance of Regnault's experiments, Watt had stated that the total heat of steam was independent of the pressure of the vapour, and therefore of the boiling point of the water.

On the other hand, Creighton and Southern had proposed the law that the amount of heat required to convert 1 gram of water at any temperature into vapour at the same temperature, was constant. If this law were true, the total heat of steam would of course increase with the elevation of the boiling point of the water.

Regnault heated his water in a boiler which could be put in communication with a pressure chamber, so that the boiling point could be varied at pleasure. The vapour formed passed downward through the boiling liquid by way of a spiral tube, and was then conveyed to the calorimeters by a tube carefully jacketed so as to prevent loss of heat. Two calorimeters similar to that represented in Fig. 69, were employed, arrangements being made so that the vapour could be passed into either at pleasure. The vapour entered into the upper copper sphere, passed down into the lower one, and then upwards through the copper worm. The pressure of the vapour was measured by means of an open mercury manometer. The water condensed in the worm or the upper copper sphere ran into the lower sphere and was drawn off into a flask and weighed.

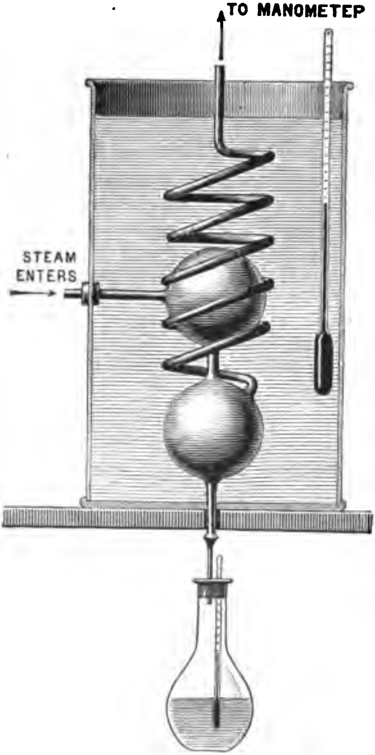

Fig. 69.—Regnault's calorimeter for determining the latent heat of steam.

Two similar calorimeters, placed side by side, were used, in order that a correction might be determined for the indirect heating, either by conduction along the steam tubes, or by radiation. Supposing both calorimeters to be exactly similar, then if the steam is passing through one and not through the other, the former will be heated by the condensation of the vapour as well as by radiation and conduction, the latter being heated only by the latter means.

It was ultimately, however, found to be best to use the method of correction explained on p. 131, only one calorimeter being used.

In this manner, employing pressures varying from ·2 to 13·6 atmospheres, Regnault determined the amount of heat,[1]

$$Q = t + L_t$$

which it was necessary to supply to 1 gram of water at 0° C., in order, firstly, to heat it to $t°$, and then to convert it into vapour at the same temperature. He found that

$$Q = 606{\cdot}5 + 0{\cdot}305t.$$

Consequently, since $Q = t + L_t$ where L_t is the latent heat of vaporisation of water at $t°$ C., we have

$$\begin{aligned} L_t &= 606{\cdot}5 + 0.305t - t \\ &= 606{\cdot}5 - {\cdot}695t. \end{aligned}$$

Consequently the latent heat of vaporisation decreases with the boiling point of water, thus disproving Creighton and Southern's law. Also, since Q increases with the boiling point t, Watt's law was disproved.

If we take $t = 100°$ C., we find the latent heat of steam boiling under standard pressure to be equal to

$$606{\cdot}5 - {\cdot}695 \times 100 = 606{\cdot}5 - 69{\cdot}5 = 537 \text{ therms per gram.}$$

When the variation of the specific heat of water is taken into account, we find the slightly smaller value 536·5 therms per gram.

Similarly the latent heat of vaporisation of water at 200° C. would be equal to 464·3 therms per gram, whilst at a temperature $t°_1$, equal to

$$\frac{606{\cdot}5}{{\cdot}695} = 872°,$$

the latent heat of vaporisation of water would have zero value.

The Steam Calorimeter.—In Black's calorimeter, described on p. 148, the specific heat of a substance is determined in terms of the latent heat of fusion of ice. The specific heat of a substance can also be determined in terms of the latent heat of vaporisation of water.

Let us suppose that a piece of metal, suspended from one end of the beam of a balance, is carefully weighed. If now by any means the piece of metal could be surrounded by "dry" steam (*i.e.* steam which does not carry fine particles of water suspended in it), heat would pass from the steam to the metal, and for every 536 therms so communicated, one gram of steam would be condensed on the metal. This condensation would proceed till the metal had attained the same temperature as the steam, when condensation would cease, unless heat is lost by radiation. The mass of the water produced by the condensation of the steam would thus increase up to a certain amount, and then remain practically constant. For if more steam were to be condensed, the temperature of the metal would be raised above that of the steam, and some of the water previously condensed would be evaporated. On the other hand, none of the water already condensed could evaporate without entailing a fall in the temperature of the metal, which would immediately occasion the condensation of an amount of steam equivalent to that which had been given off.

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[1] See Note on p. 161.

If the body is once more weighed, the mass of the water which has been condensed may be determined by subtraction.

Let w_1 = mass of the substance, the specific heat s of which is sought.
,, $t°$ C. = the initial temperature of the substance.
,, w_2 = mass of steam condensed.

Then the heat which has been communicated to the substance = $sw_1(100 - t)$.

The heat which has been given up whilst w_2 grams of steam at 100° C. condensed to water at 100° C. = Lw_2, where L = the latent heat of steam at 100° C. = 536·5 therms per gram.

$$\therefore sw_1(100 - t) = Lw_2.$$

$$\therefore s = \frac{Lw_2}{w_1(100 - t)}.$$

Certain practical difficulties have prevented the experimental application of these principles until recently. The method by which these difficulties have been overcome may be best illustrated by a description of Joly's method of determining the specific heat of gases at constant volume.

Joly's Differential Steam Calorimeter.—Specific Heat of a Gas at Constant Volume.—Two hollow spheres, made from copper as thin as is consistent with the possession of the necessary strength, are hung from the ends of a balance beam by means of fine platinum wires (Fig. 70). The spheres are enclosed by a chamber which can be filled with dry steam. They are so constructed that, when exhausted, their thermal capacities (or water equivalents) are exactly equal. Hence, if the beam of the balance be brought into equilibrium by placing weights on one of the pans, supplemented by the use of a rider, the equilibrium will be preserved when the containing vessel is filled with steam, since equal masses will be condensed on the two spheres. Small light trays are hung under both spheres in order to catch any drops of water which may fall off.

One of the spheres is now filled with a gas under pressure, and the mass of this gas determined by adding weights, &c., the vessel surrounding the spheres being meanwhile filled with air. When everything has had time to acquire a constant temperature, this latter is noted by the aid of a delicate low-range thermometer.

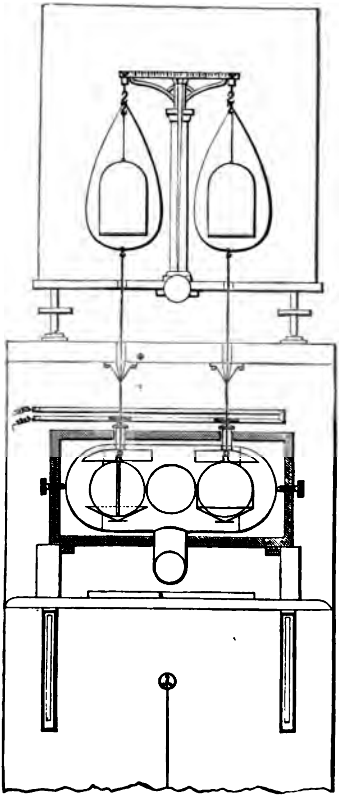

FIG. 70.—Joly's differential steam calorimeter. (P.) (Front view.)

Steam is then allowed to enter the vessel surrounding the spheres. Although the thermal capacity of the compressed gas is small, the difference in the mass of water condensed on the two spheres is quite definite, and may be accurately determined. The gas has meanwhile been maintained at a volume which is practically constant; hence the specific heat of the gas at constant volume may be directly calculated.

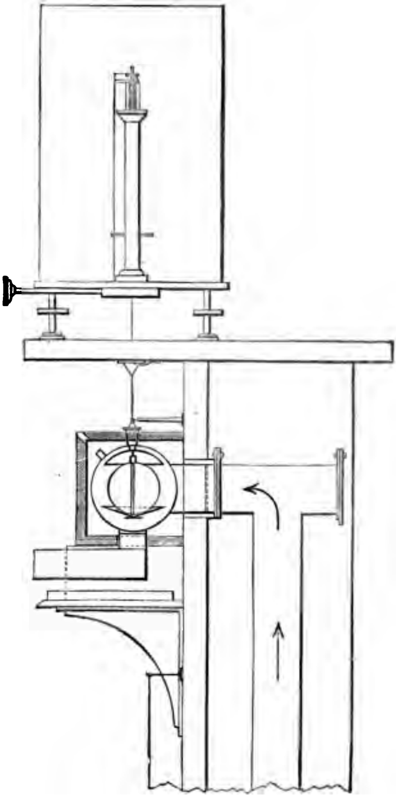

FIG. 71.—Joly's steam calorimeter. (P.) (Side view.)

One of the difficulties met with in the design of this apparatus was connected with the apertures in the steam vessel through which pass the fine platinum wires which support the spheres. If these apertures were made large, a constant stream of steam issued forth, and this precluded accurate weighing. If, on the other hand, the apertures were made small, drops of water condensed in them, and the capillary forces exerted on the wires produced considerable errors.

The method finally adopted was to make the small holes in plaster of Paris, which, being an absorbent substance, prevented the formation of drops. Small coils of platinum wire also surrounded the wires just above the holes in the plaster, and these were rendered red hot by the passage of an electric current. By these means the difficulties mentioned were completely surmounted.

Joly found the mean specific heat of hydrogen to be 2·402. The value of the specific heat decreased with the density. The value found for the specific heat of air at a pressure of 19·5 atmospheres was 0·1721, and that of carbon dioxide gas varied from 0·16841 at a pressure of 7·2 atmospheres to 0·17386 at 21·66 atmospheres.

Specific Heat of a Gas at Constant Pressure (Regnault's Experiments).—Although the method used by Regnault, in determining the specific heat of a gas under constant pressure, was in no way dependent on the principles

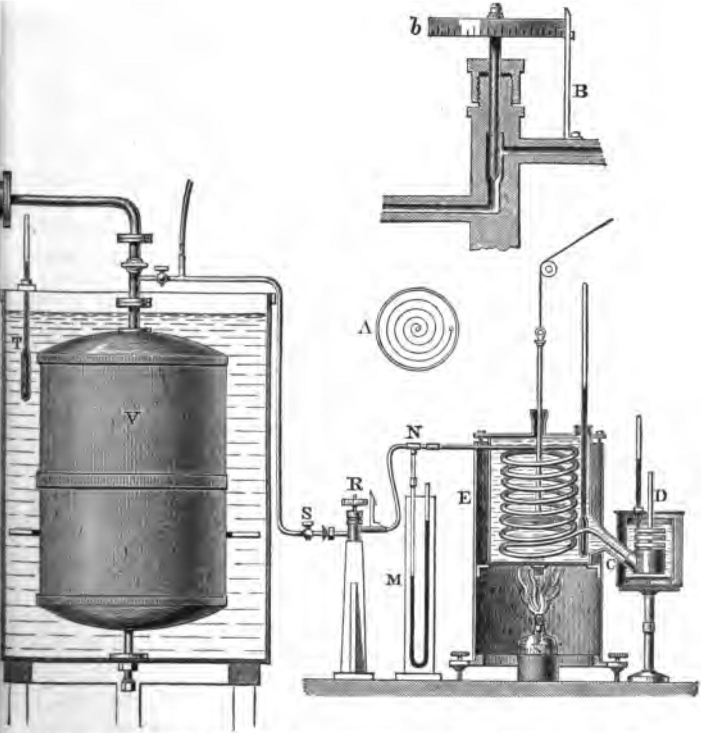

Fig. 72.—Regnault's apparatus for determining the specific heat of a gas under constant pressure. (P.)

developed in this chapter, the present is perhaps the most fitting occasion to describe these experiments.

It will be explained later (see Chap. XIII.) why a gram of gas should require more heat to raise its temperature through 1° when the pressure remains constant, than when the volume is maintained invariable. It need only be remarked here, that when the pressure of a gas remains constant, any rise of temperature will be accompanied by an increase of the volume of the gas. It is a well-known fact that if a gas is allowed to suddenly expand, its temperature will be lowered, and therefore heat must be supplied to raise it to its initial temperature. Thus if a gram of gas were heated at constant volume through 1° C., a certain amount of heat, termed the specific heat of the gas at constant volume, would be absorbed. If it were then allowed to expand till its pressure reached the value it originally possessed, the gas would be cooled, and hence additional heat would be required to raise its temperature to the value that it had before the expansion took place.

In order to determine the value of the specific heat of a gas under constant pressure, Regnault allowed a stream of heated gas to pass through a spiral tube contained in a copper vessel filled with water, and observed the consequent rise in temperature of the water.

The gas to be experimented on was stored in a reservoir V (Fig. 72), which was maintained at a constant temperature. The quantity of gas which passed through the calorimeter during an experiment was determined from measurements made of the initial and final pressures of the gas in V.

The gas was heated whilst passing through a long spiral tube of copper immersed in an oil-bath E. In order to maintain a steady flow of gas, its pressure, immediately before entering this spiral, was indicated by a manometer M, and was maintained constant by opening the valve R as the pressure in V diminished. After having been heated to the temperature of the bath E (which was read by the aid of the thermometer shown), the gas passed directly through a spiral copper tube immersed in water in the calorimeter C. A water manometer, not shown in Fig. 72, was used in order to be sure that the pressure of the gas had not altered appreciably whilst passing through the calorimeter.

In performing an experiment, the rate of rise of temperature of the calorimeter was ascertained just before passing the heated gas through it. The heated gas was then allowed to stream through it till the temperature had risen by a certain amount, which was carefully observed. The gas was then turned off, and the rate of change of temperature of the calorimeter was again determined. The first and third observations were made in order to obtain data for applying a correction for the heat gained or lost by radiation and conduction. (See method explained on p. 131.)

NOTE.—Prof. Callendar and others have pointed out that Regnault's determination of the Latent Heat of Steam, though far in advance of his time, requires revision when considered in the light of recent advances. It has been objected,

(1) That his thermometry was imperfect.

(2) The variation of the specific heat of water, between 0° and 60° (see p. 135) was unknown to him.

(3) Regnault admitted that the observations below 175°C. were vitiated by an escape of steam into the idle calorimeter.

In addition, the Latent Heat of Water should become equal to zero at the critical temperature (see Ch. IX.) which is 365°C., instead of 872°, as calculated from Regnault's formula.

The latest values for the Total Heat (Q) and the Latent Heat (L) of steam, due to Prof. Callendar, are given in the 4th and 5th columns of the table on p. 467 at the end of this book.

SUMMARY.

The Latent Heat of Fusion of a substance is the quantity of heat required to convert one gram of the substance from the solid to the liquid state, no change meanwhile occurring in its temperature.

The Latent Heat of Fusion of Ice may be determined by placing a known mass of ice in a known mass of warm water, and observing the consequent fall of temperature of the water.

Black's Ice Calorimeter consists of a hollow vessel of ice. The specific heat of a solid can be determined by heating it to a definite temperature, placing it in the ice calorimeter, and determining the mass of ice converted into water at 0°C.

The Latent Heat of Vaporisation of a substance is equal to the quantity of heat required to convert one gram of the substance from the state of liquid to that of vapour at the same temperature.

The Total Heat of Steam at t° C. is the quantity of heat which must be communicated to one gram of water, initially at 0° C., in order to convert it into saturated vapour at a temperature of $t°$ C.

Regnault found that the total heat of steam increased with the temperature of vaporisation. The latent heat of steam decreases with the temperature of vaporisation, and would, according to Regnault's formula, be equal to zero at 872° C.

Joly's Steam Calorimeter.—By the aid of this instrument the specific heat of a solid is determined by observing the amount of steam at 100° C. which is condensed to water at 100° C. in raising the temperature of a known mass of the solid from some definite temperature to 100° C.

SPECIFIC HEATS OF GASES.

The Specific Heat of a Gas at Constant Volume has been determined by Joly by the aid of his differential steam calorimeter.

The Specific Heat of a Gas at constant pressure has been determined by Regnault, by causing a known mass of heated gas to be cooled in passing through a known mass of water.

The specific heat of a gas at constant pressure is always greater than the specific heat of the gas at constant volume.

QUESTIONS ON CHAPTER VII.

(1) Explain the method of determining the latent heat of vaporisation of a liquid, and describe the apparatus you would employ.

(2) Water contained in a closed calorimeter is heated and the heat supplied is measured. The vapour formed is removed at such a rate that the temperature of the liquid remains constant. Hence, show how to find the latent heat of evaporation of the liquid.

(3) How may the specific heat of a gas at constant pressure be accurately determined?

(4) Describe Joly's steam calorimeter and his investigation of the specific heats of gases at constant volume.

(5) Describe a method of finding directly by experiment the specific heat of a gas at constant pressure.

(6) Describe and explain the method of using Joly's steam calorimeter.

(7) Define latent heat. How much ice at 0° C. would a kilogram of steam at 100° C. melt if the resulting water was at 0° C.?

(8) A piece of iron weighing 16 grams is dropped at a temperature of 112·5° C. into a cavity in a block of ice, of which it melts 2·5 grams. If the latent heat of ice is 80, find the specific heat of iron.

(9) Define what is meant by the "latent heat" of water, and state exactly how you will proceed to measure it experimentally.

(10) Define the specific heat of a gas at constant pressure and at constant volume, and describe some method of measuring one of these quantities. Why is the first of these quantities always greater than the second?

(11) What is meant by the statement that the latent heat of water is 80?

The temperature of a pond is 8° C. when a freezing wind sets in. Describe what happens as the water parts with its heat, and assuming that it parts with it at a uniform rate, compare the time taken to the beginning of freezing with the time taken to freeze the top half-inch of water, the total depth being 20 inches.

(12) Define latent heat of vaporisation.

One pound of hot water is poured into a shallow polished vessel supported on three corks, and whilst 0·25 ounce is evaporating the temperature falls from 90° to 80° C. Neglecting heat lost by radiation, convection, and conduction, calculate the latent heat of vaporisation of water.

(13) Describe Regnault's method of determining the specific heat of a gas under constant pressure, and state the general results obtained.

(14) Describe Joly's steam calorimeter and his investigation of the specific heat of gases at constant volume.

PRACTICAL.

(1) Find the latent heat of steam.

(2) Find the latent heat of fusion of ice.

CHAPTER VIII

CHANGE OF STATE

FUSION

Cooling Curves.—EXPT. 40.—Take a thin-walled boiling tube and half fill it with distilled water. Obtain a thin-walled test tube, of such a diameter that it will just admit of a thermometer being placed in it, and fill the free space surrounding the thermometer bulb with mercury. Place the test tube and thermometer in the boiling tube (Fig. 73), and then place the whole arrangement in a beaker containing a freezing mixture made from ice and salt. Read the temperature indicated by the thermometer every half minute, and finally plot your observations, measuring time horizontally and temperature vertically.

You will thus obtain a cooling curve of the general form shown in Fig. 74. It will be noticed that, after falling to 0° C., the temperature remains constant for a considerable interval, and then recommences to fall.

The meaning of this stationary temperature at 0° C. may be easily explained. When the distilled water has cooled to 0° C., solidification commences. But for every gram of water which solidifies, 80 therms of heat will be given up. On the other hand, the colder mixture of ice and salt is continually abstracting heat from the water in the test tube. The water will solidify at such a rate that the heat given up during solidification is just balanced by the heat abstracted by the freezing mixture, the temperature of the freezing water meanwhile remaining stationary.

When the whole of the water has solidified, cooling will recommence. When no further fall of temperature is indicated by the thermometer, remove the boiling tube with its contained ice, and place it in a beaker half filled with water which is kept at a constant temperature of about 30° C., by heating, when necessary, with a Bunsen burner. The thermometer will now be found to indicate a rising temperature till 0° C. is reached; it will then remain at the latter temperature till all the ice has disappeared, when a further rise in temperature will take place till 30° C. is reached.

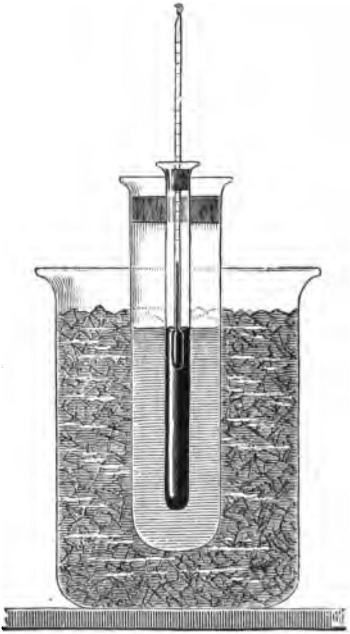

FIG. 73.—Arrangement for determining the cooling curve of water.

One of the most convenient methods of determining the melting point of a solid is to allow the melted substance to cool, and to draw a cooling curve from the observations of the temperature made at short intervals of time. Crystalline substances show a well-marked horizontal portion of this curve, which indicates the melting point. Substances like paraffin wax, which in solidifying pass through an intermediate pasty condition, exhibit a less abrupt alteration in the rate of cooling in the neighbourhood of the melting point.

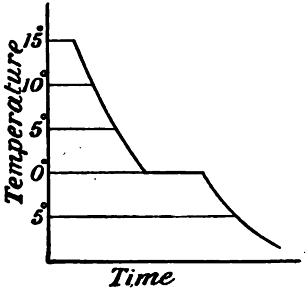

FIG. 74.—Cooling curve for water.

When mixtures of metals are melted and allowed to cool, two or more stationary temperatures may be observed, indicating that the different metals solidify at different temperatures.

Expt. 41.—*Obtain the cooling curve for paraffin wax.*—Heat some wax contained in a test tube to about 60° C.; place a thermometer in it, and regularly observe the temperature at short intervals. Plot the curve in the manner already explained.

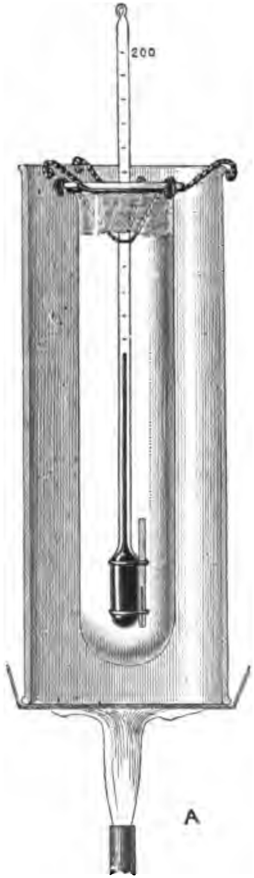

Fig. 76.—Arrangement for determining the melting point of a solid.

To determine the Melting Point of a Substance.—

Expt. 42.—*To determine the melting point of sulphur.*—Introduce a little powdered sulphur into a piece of capillary tube closed at its lower end. Fasten this piece of capillary tube by the side of the bulb of a thermometer reading to 200° C., by the aid of pieces of thin wire. Support the thermometer within a rather wide boiling tube, the upper end of which is filled up with a plug of glass wool. The air in the tube is heated by means of a gas flame. The wider tube (Fig. 76) serves to equalise the temperature along the whole height of the thermometer. The thermometer and test tube are supported by wires in the manner indicated in Fig. 75. The lower end of the outer tube is preferably covered with a piece of iron wire gauze.

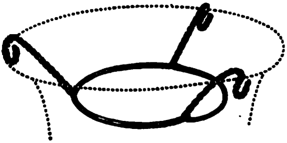

Fig. 75.—Method of supporting the test tube shown in Fig. 75.

Notice the temperature when the first indications of melting are exhibited. This will be the melting point of the sulphur.

Overcooling.—Under certain conditions it is possible to cool water to a temperature considerably below 0° C. without solidification occurring. Fahrenheit found that water, enclosed in a thermometer-shaped vessel which had been freed from air, could be cooled below the freezing point of water without any ice being formed. When, however, the stem was broken, solidification rapidly set in. Gay-Lussac cooled water to – 12° C. without solidification taking place, the surface of the water being covered with a layer of oil. A small fragment of ice dropped into the overcooled water caused solidification to commence, the temperature quickly rising to 0° C.

This property is not peculiar to water, but is exhibited by most other substances. If, for instance, phosphorus is melted in a U tube, its free surfaces being covered with water, it may be cooled considerably below 44° C., which is its normal melting point, without solidification occurring. If a small fragment of solid yellow phosphorus is then dropped into one of the limbs of the U tube, solidification will commence at this fragment, and spread along the tube, the temperature of the phosphorus rising meanwhile to 44° C. A fragment of amorphous red phosphorus will not start solidification. The rate at which the solidification travels along the tube is greater in proportion to the degree of overcooling.

From this experiment we learn two facts of great importance :—

1. Solidification takes place only at the surface of the solid already formed.
2. The rate at which solidification takes place at a given surface is proportional to the degree of over-cooling.

Beckmann's Freezing Point Apparatus.—The fact that the temperature of an over-cooled liquid rises to the freezing point when solidification occurs, has been made the basis of a method of determining freezing points. Beckmann's apparatus is shown in Fig. 77. It consists of a test tube A, provided with a side inlet tube D, and a cork through which a thermometer T and a platinum wire stirrer S_2 pass. This test tube is surrounded by a larger tube B, the space between the two forming an air jacket. Both are surrounded by a larger vessel C, which can be filled with a suitable freezing mixture. The latter is kept in circulation by means of the wire stirrer S_1.

The method of using the above apparatus is as follows :—

Some of the liquid of which the freezing point is required, is introduced into A, by way of the inlet tube D, which is afterwards closed by a cork. A suitable freezing mixture is introduced into C, and the whole apparatus is allowed to stand till the thermometer T indicates a temperature one or two degrees below the probable freezing point of the liquid. The platinum wire stirrer S_2 is then moved briskly up and down, when solidification will generally occur. The temperature indicated by T rises and shortly attains a value which remains constant for some time. This temperature is the freezing point of the liquid.

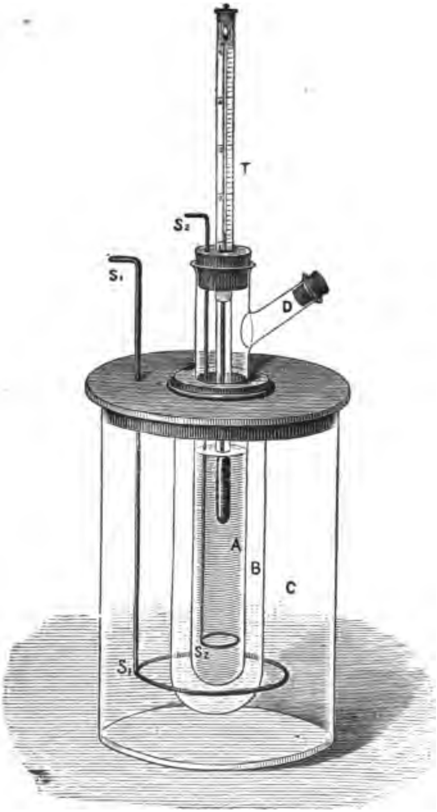

FIG. 77.—Beckmann's apparatus for determining the freezing point of a solution.

The Freezing Point of a Solution is always lower than that of the pure Solvent.

A common method of removing ice from pavements is to sprinkle salt upon it. The mixture of salt and ice is incapable of remaining solid unless its temperature is much below 0° C. Consequently the ice melts, and the heat absorbed in this process causes the temperature to fall till the freezing point of the mixture is attained.

The use of a mixture of ice and salt as a freezing mixture will be explained later on.

An aqueous solution of *any substance* will possess a freezing point lower than 0° C.. The following table, taken from Lüpke's *Elements of Electro-Chemistry*, exhibits the depression of the freezing point produced by dissolving definite quantities of cane sugar in water.

Mass of Cane Sugar dissolved in 100 grms. of Water.	Freezing point.	Depression of the freezing point, per grm. of dissolved Sugar.	Molecular depression of the freezing point.
	° C.	° C.	° C.
34·2	−1·8	0·053	18·13
51·3	−2·8	0·054	18·45
68·4	−3·8	0·056	18·81

The third column in the above table is obtained by dividing the depression of the freezing point by the corresponding mass of sugar dissolved in 100 grams of water. The numbers so obtained are very nearly constant, and would be more nearly so if the solutions had been more dilute. Hence we arrive at the law that *the freezing point of a dilute solution of a particular substance is depressed below that of the pure solvent by an amount proportional to the concentration of the solution.*

By the concentration of the solution, we mean the mass of the dissolved substance per 100 grams of the solvent.

In order to understand the connection between the freezing point depressions produced by various substances, the meaning of the term molecular weight must be firmly grasped.

If we take the mass of an atom of hydrogen as 1, then the mass of a molecule of hydrogen will be equal to 2. The mass of a molecule of water will be equal to $(16 + 2) = 18$. Similar reasoning may be applied to other substances. From this it follows that 2 grams of hydrogen will contain as many molecules as 18 grams of water. More generally, we may say that masses equal to the respective molecular weights of various substances will contain equal numbers of molecules.

The freezing point depression produced by dissolving one gram of any substance in 100 grams of water may be obtained experimentally by the use of Beckmann's apparatus. This operation has been performed for a large number of substances. If the values so obtained are multiplied by the respective molecular weights of the dissolved substances, we obtain the depressions produced by dissolving equal numbers of molecules of those substances in equal masses of water. These values are termed the *molecular depressions of the freezing point.*

The following table gives the molecular depressions of the freezing point of water for a number of dissolved substances. The numbers are taken from Ostwald's *Solutions.*

AQUEOUS SOLUTIONS.

Dissolved Substance, Class I.	Molecular Depression.	Dissolved Substance, Class II.	Molecular Depression.
	°C.		°C.
Methyl alcohol . .	17·3	Hydrochloric acid	39·1
Ethyl ,, . .	17·3	Nitric . ,,	35·8
Glycerine	17·1	Sulphuric ,, .	38·2
Cane sugar . . .	18·5	Caustic potash . .	35·3
Acetic acid . . .	19·0	Caustic soda . .	36·2
Tartaric ,, . . .	19·5	Potassium chloride	33·6
Citric ,, . . .	19·3	Sodium chloride	35·1
Average molecular depression . . .	18·3	Average molecular depression . . .	36·2

An examination of the above table shows that substances soluble in water may be divided into two classes, according to their molecular behaviour in depressing the freezing point. In the first class, of which cane sugar is a typical example, the molecular depression is practically constant, and has an average value of 18·3° C. Thus, *solutions containing equal numbers of molecules of the various substances in Class I., dissolved in equal masses of water, will possess the same freezing point.*

The substances in this class, when dissolved in water, form electrically non-conducting or badly conducting solutions.

Solutions of the substances in the second class are good electrical conductors. The average molecular depression of the freezing point amounts to 36·2° C., very nearly double of that obtaining in the first class. Thus, we see that a solution comprising a given number of molecules of caustic soda in 100 grams of water will possess the same freezing point as a solution comprising *double* the number of molecules of cane sugar in 100 grams of water.

This has led to the hypothesis that substances similar to those in Class II. become dissociated, or split up into simpler elements, when dissolved in water. Thus potassium chloride, when dissolved in water, is supposed to be split up into separate atoms of potassium and chlorine respectively. This assumption has received considerable support from study of the electrical conductivities of solutions.[1]

Crystallisation of Super-saturated Solutions.—EXPT. 43.—Add crystallised sodium sulphate to boiling water till no more will dissolve. Pour the hot solution into a clean flask, place a thermometer with its bulb in the solution, and plug up the mouth of the flask with cotton wool. Place the flask where it will be free from disturbances or mechanical vibrations till the solution has cooled to the temperature of the room. You will then have a super-saturated solution of sodium sulphate. If a small crystal of the same substance be dropped into the liquid, crystallisation will occur, a considerable rise in temperature being indicated by the thermometer. The heat given up by the sulphate in crystallising bears an obvious resemblance to the latent heat of fusion of ice.

Freezing Mixtures.—We have seen that when sodium sulphate crystallises out from a supersaturated solution, a considerable rise in temperature occurs, indicating an evolution of heat. Conversely, heat is absorbed and the temperature lowered, when sodium sulphate is dissolved in water. If the crystals are finely powdered to start with, and are added to tolerably cold water, a temperature as low as −15° C. can be obtained.

If ice and common salt are mixed, the temperature of the liquid produced may fall to −22° C. If four parts (by weight) of crystalline calcium chloride are added to three parts (by weight) of ice, a temperature of −55° C. can be obtained.

Freezing of Salt Solutions.—Guthrie found that if a dilute solution of salt and water is gradually cooled, a small quantity of pure ice is formed at some temperature below 0° C., which varies with the strength of the solution. As the temperature falls, more ice separates out, the salt solution thus becoming more concentrated. At a certain point the solution becomes saturated, and the whole then crystallises out. This always happens at −22° C. The substance finally obtained appears to be a definite chemical compound, analysis always yielding results of the form of $NaCl + nH_2O$. It is termed a **Cryohydrate.** If a saturated salt solution be taken to start with, crystals of cryohydrate are deposited as it is cooled, the whole finally becoming solid at −22° C. This is the limiting temperature to which a salt solution can be cooled without solidification occurring. As the success of a freezing mixture, made from a mixture of ice and salt, depends on the constituents dissolving, −22° C. is the lowest temperature which can be obtained by this means.

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[1] The student wishing to pursue this subject further is referred to Lüpke's *Electro-Chemistry*, Whetham's *Solution and Electrolysis*, Nernst's *Theory of Chemistry*, or the works of Ostwald.

Change of Volume on Solidification.—Many substances contract on solidification. Solid paraffin wax sinks to the bottom of liquid paraffin wax, thus showing that its density is greater, and consequently that the volume of a given mass is smaller in the solid than in the liquid state. The deep depression in the surface of paraffin wax which has been allowed to cool in an open vessel is due to the same cause. Aluminium contracts to such an extent during solidification, that special precautions must be taken in casting with that metal, in order to prevent the formation of holes. On the other hand, water, bismuth, type metal (a mixture of lead and bismuth), and several other substances expand during solidification.

The expansion of water during freezing is answerable for the bursting of pipes and the occasional splitting of trees, but also serves the useful purpose of disintegrating hard soils. Ponds and lakes freeze from the surface downwards, owing to the facts that 4° C. is the temperature of maximum density of water, and that ice is less dense than water at 0° C.

The sharpness of outline necessary for printing type could not be obtained, except for the fact that type metal in solidifying expands and fills every corner of the mould. Cast iron assumes a pasty condition before solidifying, expanding at the same time; subsequently a contraction takes place. Much of the perfection attainable in iron castings is due to the former fact. The surface of an iron casting will often exhibit a complete copy of the grain of the wood used in making the pattern.

Bunsen's Method of Determining the Expansion of Water on Solidifying.

EXPT. 44.—Take a piece of glass tubing, about a foot long and of about $\frac{1}{2}''$ internal diameter, and draw one end out into a fine capillary tube. Subsequent success will largely depend on the walls of this capillary tube being thick near the junction with the larger tube. Hence the glass should be well melted, being continually turned in a hot blowpipe flame, to allow the glass to thicken up before it is pulled out.

The large tube is then heated at a distance of about six inches from the commencement of the capillary tube, and after being slightly drawn out, is bent into a U as shown in Fig. 78. No great difficulty will be found in this operation if the glass is well heated and allowed to thicken before being pulled out. A constriction is made at A, and the capillary tube is bent at D near its junction to the wider tube, as shown in the figure.

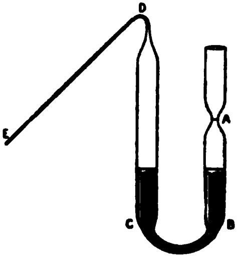

FIG. 78.—Apparatus for determining the expansion of water on freezing.

Pour some clean mercury into the open end of the tube till it stands at a height of two or three inches in either limb. Run this mercury backwards and forwards to remove any air bubbles clinging to the glass. Weigh the tube and mercury, and write down the value you obtain.

Boil some distilled water in a beaker for several minutes so as to expel the dissolved air. Then place the end E of the capillary tube DE below the surface of this water, and tilt the U-tube so that an excess of mercury runs into the tube DC. On bringing the limbs of the U-tube into a vertical position, water will run into DC through the capillary tube. Repeat these operations till the space above the mercury in DC is entirely filled with water. It is best to subsequently boil this water by heating the tube DC with a Bunsen burner, so as to expel the last traces of dissolved air.

Clamp the U-tube in a vertical position, the end of the capillary tube still remaining under water. Heat the capillary tube gently just below D with a mouth blow-pipe ; when the water near this point has been converted into steam, increase the temperature of the flame till the tube fuses, when the capillary tube may be pulled off. Expel the water from this capillary tube, and weigh it together with the U tube and its contents. You can thence obtain the mass of the enclosed water.

Pour mercury into the open end of the U-tube till its surface is about level with a scratch previously made on the tube at the constriction A. Then place the whole arrangement in a beaker filled with clean snow or ice shavings. After it has stood long enough for you to feel satisfied that the contents have reached 0° C., pour mercury in till the surface is exactly level with the scratch in the constriction.

In order to freeze the water, a small paper funnel is placed over the end D of the limb DC which contains the water, and a mixture of calcium chloride and ice is poured into this funnel. When freezing has commenced, a little calcium chloride should be added to the ice surrounding the U-tube. The water will then solidify downwards, thus avoiding any risk of fracture from the expansion of the water in freezing. The ice formed should be quite clear, and free from striations or air bubbles.

When the freezing has been completed, quickly wash the outside of the tube in *ice cold* water, and then place the whole arrangement in a beaker, and surround it with pure snow or ice shavings. It should be left there for nearly an hour to ensure that the whole of the contents have once more reached a temperature of 0° C. It will then be found that the surface of the mercury stands at some distance above the scratch in the constriction A. Transfer this mercury, by the aid of a small pipette, into a weighed watch glass, leaving the surface once more level with the scratch. Obtain the mass of the mercury you have removed. The volume occupied by this mass of mercury at 0° C. will be equal to the increase of volume undergone by the contained water at 0° in changing to ice at 0°. 1 gram of mercury at 0° C. occupies a volume of 0·073553 c.cs. 1 gram of water at 0° C. occupies a volume of 1·00013 c.cs.

Finally, you must calculate the increase in volume experienced by 1 c.c. of water at 0° C. in changing into ice at 0° C.

Bunsen found that 1 c.c. of water at 0° C. occupied a volume of 1·090 c.c. when frozen. Roughly we may say that ten volumes of water at 0° C. occupy eleven volumes at the same temperature when frozen.

Erman and Kopp's Experiments.—A quantity of ice was contained in a thermometer bulb, a liquid which did not mix with water filling the remainder of the bulb and part of the stem. The apparent expansion of the liquid in the bulb being known, the volume changes undergone by the ice, either when cooled below 0° C. or heated to a higher temperature, could be determined. It was found that ice contracts when cooled below 0° C., its mean co-efficient of expansion per degree centigrade being 0·000057. The change in volume on melting was found not to take place suddenly, but to follow a curve, such as Fig. 79. This curve is not, however, drawn to scale, but is intended only to indicate the nature, and not the extent of the volume changes.

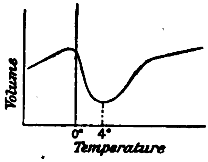

FIG. 79.—Volume changes of water near its freezing point.

Many other substances showed a similar contraction on melting.

Force called into play by the Expansion of Water on Freezing.—When water is frozen the force called into play by the change of volume will burst strong metal vessels.

EXPT. 45.—Seal one end of a glass tube of about $\frac{1}{2}''$ diameter, and draw the other end out into a thick-walled capillary tube. Fill the vessel so formed with water in the manner detailed, when the method of filling a weight thermometer was described (p. 87). Allow the water to cool, and then seal off the capillary tube. Place the vessel in a wooden bowl, and surround it with a mixture of ice and salt. Cover the bowl with a duster to prevent the possibility of pieces of the glass being projected into the room. After a few minutes the bursting of the tube will be announced by a characteristic noise.

In a similar manner cast-iron shells can be burst.

Bunsen's Ice Calorimeter.—A measurement of the alteration which occurs in the volume of a certain quantity of ice and water at 0° C., may be used to determine the amount of ice which has been melted, and hence the quantity of heat which has been communicated to the mixture. Bunsen's Ice Calorimeter, Fig. 80, is designed on these principles.

A cylindrical test tube A is surrounded by a larger cylindrical glass vessel BC, the two being fused together at B. The lower end of BC is connected to a bent tube CDEF, furnished with a collar at F.

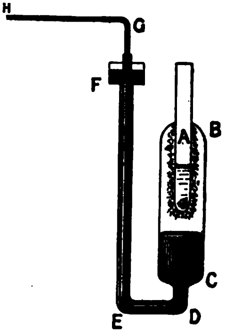

FIG. 80.—Bunsen's ice calorimeter.

The upper part of the vessel BC is filled with pure distilled water, some of which has been frozen into an ice sheath surrounding the inner test tube. Below this water, and filling the tube DEF, is pure mercury. A fine graduated capillary tube GH is pushed through a cork closing the upper end of EF. The mercury meniscus can be brought to any point in GH, by pushing the capillary tube further through the cork, or withdrawing it, as the case may require.

The water is initially introduced into BC by inverting the apparatus, placing the end F of the tube EF below the surface of boiling distilled water, and alternately heating and cooling BC. The water in BC is finally boiled to remove any trace of air. The end F of the tube EF is then placed beneath the surface of some pure mercury, and some of the water in BC is boiled off. On cooling, mercury fills the lower part of BC and the tube EF.

In order to freeze the ice sheath, it is best[1] to cool the whole apparatus to 0° C., and then to introduce some solid carbon dioxide into the inner tube. This produces intense *local* overcooling, and consequently some ice crystals separate out. The ice sheath is then made to grow to the required size by pouring ether into the tube A and blowing a current of air through it. These precautions are necessary, since ice does not commence to form until a temperature far below 0° C. has been attained (see p. 167), whilst when the ice has once commenced to separate out, if the whole of the water in BC is at the same low temperature, the freezing may take place with sufficient rapidity to burst the vessel.

The whole of the apparatus is then surrounded with *pure* snow; if ice shavings are used these will generally be at a temperature slightly below 0° C., owing to the presence of impurities, so that a progressive freezing will take place in the water in BC.

Errors from this cause may be avoided, as was suggested by Prof. C. V. Boys, by separating the ice shavings from the walls of the vessel BC by means of an air jacket.

A small amount of water or other liquid at 0° C. is introduced into the tube A. In determining specific heats, a small weighed quantity of a solid is heated to any desired temperature, and then quickly dropped into the water in A. As the density of water increases up to 4° C., the heated water will sink to the bottom of A, and communicate its heat to the ice sheath, some of which will consequently be melted. The amount melted is determined by noticing the initial and final position of the meniscus in GH.

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[1] Mond, Ramsay, and Shields, "On the Occlusion of Oxygen and Hydrogen by Platinum Black," Part II., *Phil. Trans.*, vol. 190 (1897), p. 131.

The necessary calculations may be performed as follows:—

From Bunsen's experiments, we know that 1,090 c.cs. of ice at 0° C. form 1,000 c.cs. of water at the same temperature. Further, 1,000 c.cs. of water at 0° C. will possess a mass of 1,000 grams (approximately). Therefore, corresponding to a decrease of volume of $(1{,}090 - 1{,}000) = 90$ c.cs., due to the melting of ice at 0° C, to water at the same temperature, an amount of heat equal to $1{,}000 \times 80 = 80{,}000$ therms must have been communicated.

Hence, finally, for a decrease of 1 c.c., as indicated by the motion of the mercury meniscus, a quantity of heat equal to $\frac{80{,}000}{90} = 888 \cdot 9$ therms must have been communicated.

With a fine capillary tube the communication of ·1 therm may produce a motion of the mercury meniscus through 1 millimetre, so that the sensitiveness of this apparatus is sufficiently manifest. It is particularly suitable for the determination of specific heats of substances of which small quantities only can be procured. Thus Weber used Bunsen's ice calorimeter to determine the specific heat of the diamond.

Effect of Pressure on the Melting Point.—In the case of a substance like water, which expands on solidifying, it is obvious from general principles that an increase of pressure will tend to oppose expansion, and therefore, presumably, to hinder the occurrence of solidification.

In other words, we might expect an increase of pressure to necessitate a lower temperature being attained before water would solidify, or that increased pressure would lower the freezing point of water.

In the case of substances like paraffin wax which contract on solidifying, we might expect an increased pressure to raise the melting point.

The theoretical investigation of the extent of this variation of the melting point with pressure was originally carried out by Professor James Thomson. An account of this will be found in Chap XVII. We will here consider only the experimental verification of the conclusions arrived at, which was undertaken by Professor James Thomson's brother, now Lord Kelvin.

A strong glass case, provided with a metal cap fitted with a screw piston E, Fig. 81, was filled with a mixture of clean ice and distilled water. A sensitive sulphuric ether thermometer, inclosed in a case A to protect it from the straining influence of high pressures, was used to determine the temperature of the mixture at any moment. A lead ring BB was used to keep a space clear from ice so that the thermometer could be read. The pressure to which the ice was subjected was read by means of a tube closed at one end, and placed, while full of air, in an inverted position in the water.

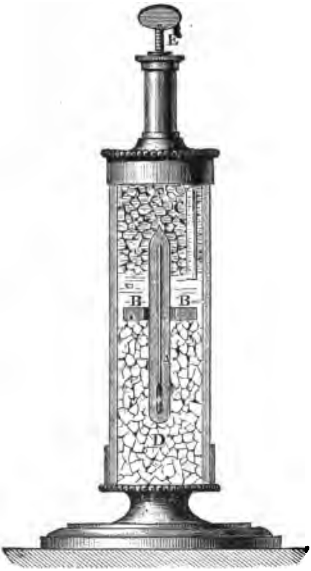

FIG. 81.—Lord Kelvin's apparatus for determining the depression of the freezing point of water by pressure. (P.)

If an increase of pressure lowers the melting point of ice, when the piston E is screwed down the contained mixture at 0° C. will be above the melting point of the ice. Thus a certain amount of ice will melt, the necessary heat being abstracted from the rest of the mixture. Consequently the temperature indicated by the thermometer will fall, till the new melting point of the ice is attained. Similarly, when the pressure is released, the thermometer will indicate a rise of temperature.

The experimental results obtained by Lord Kelvin are contained in the following table:—

Pressure observed.	Fall of temperature observed.	Fall of temperature calculated.	Difference.
8·1 atm.	0·106° F.	0·109° F.	−0·003° F.
16·8 ,,	0·232° F.	0·227° F.	+0·005° F.

Professor Dewar has more recently determined the depression of the melting point of ice as 0·0072° C. per atmosphere increase of pressure.

Bunsen has found that paraffin wax, which melted at 46·3° C. under atmospheric pressure, melted at 49·9° C. under a pressure of 100 atmospheres.

Regelation.—

EXPT. 46.—Take two pieces of ice and press them closely together. On releasing the pressure it will be found that they are frozen on to each other. This will occur even when the pieces of ice are pressed together under warm water.

Faraday was the first to notice the peculiar property of ice determined from the above experiment. The explanation is quite obvious when we remember that at the point where the pieces of ice are pressed together, the melting point of the ice will be lowered by the pressure, and some of the ice will melt, the temperature in the neighbourhood of the point meanwhile falling. On releasing the pressure the freezing point of the water will rise, and the water will solidify.

EXPT. 47.—Take a block of ice about 12″ × 8″ × 8″, and support it so that it bridges across the space between two tables. Pass a loop of thin copper wire, to which is attached a mass of about 28 lbs., over the block of ice. It will be found that the wire slowly cuts its way through the ice, without, however, dividing the block into two pieces.

The explanation of this experiment is as follows:—The ice immediately under the wire is subjected to a considerable pressure, so that its melting point is reduced and liquefaction takes place. The wire, of course, displaces the water formed, the latter solidifying as soon as it has reached the other side of the wire, and the pressure to which it was subjected is removed.

We thus have ice melting under the wire, accompanied, of course, by a fall of temperature, whilst solidification is continually taking place above the wire accompanied by a corresponding rise of temperature. It is clear that if heat can be conducted from the upper to the lower side of the wire, the rapidity with which the latter moves will be increased. This explains why a copper wire, which is a good conductor of heat, will cut through the ice more quickly than an iron wire, which is a very much worse conductor. A piece of string will not cut through the ice at all.

When snow is pressed in the hands, it can be converted into a solid block of ice, provided its temperature is not below 0° C. If the temperature of the snow were -1° C., a pressure of 143 atmospheres would be required to liquefy it. Consequently, in keenly frosty weather snowballs cannot be made, though the pressure of the wheels of a heavy cart may leave lines of ice along the road.

Snow or powdered ice, enclosed in a suitable vessel, may be converted into a mass of clear transparent ice by the application of pressure.

Skating.—Professor Joly[1] has pointed out that to the above phenomena, depending on the lowering of the melting point of ice by pressure, may be added those attending skating, *i.e.*, the freedom of motion and, to a great extent, the "biting" of the skate.

The pressure under the edge of a skate is very great. The blade touches for a short length of the hog-back curve, and, in the case of smooth ice, along a line of indefinite thinness, so that until the skate has penetrated some distance into the ice the pressure obtaining is great; in the first instance, theoretically infinite. But this pressure involves the liquefaction, *to some extent*, of the ice beneath the skate, and penetration or "bite" follows as a matter of course. As the blade sinks, an area is reached at which the pressure is inoperative, *i.e.*, inadequate to reduce the melting point below the temperature of the surroundings. Thus, estimating the pressure for that position of the edge when the bearing area has become $\frac{1}{50}$ of a square inch, and assuming the weight of the skater as 140 lbs., and also that no other forces act to urge the blade, we find a pressure of 7,000 lbs. to the square inch, or 466 atmospheres, sufficient to ensure the melting of the ice at $-3{\cdot}5^\circ$ C. With very cold ice, the pressure will rapidly attain the inoperative intensity, so that it will be found difficult to obtain "bite"—a state of things skaters are familiar with. But it would appear that *some* penetration must ensue. On very cold ice, "hollow-ground" skates will have the advantage.

This explanation of the phenomena attending skating assumes that the skater, in fact, glides about on a narrow film of water, the solid turning to water wherever the pressure is most intense, and this water, continually forming under the skate, resuming the solid form when relieved of pressure.

Formation of Glaciers.—Snow accumulates to great depths at points above the snow line, so that the lower layers, which are subjected to great pressures due to the superincumbent masses, are melted and squeezed out, solidification taking place as soon as the water formed has escaped. Thus, in high mountains we have huge streams of ice continually supplied from the snow above the snow line.

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[1] *Nature*, March 23, 1899. *Proc. Roy. Dublin Society*, vol. v. p. 453, 1886.

Motion of Glaciers.—Glaciers are found to move down the sides of mountains, the upper layers moving faster than the lower ones, and the centre more quickly than the sides. Three main theories have been proposed to account for this motion.

1. The action of gravity will of course produce great pressures in certain parts of the ice, and at these points liquefaction will occur, solidification taking place when the motion of the ice has relieved the strain. According to this view, which was strongly advocated by the late Professor Tyndall, the motion of a glacier is entirely due to the liquefaction of the ice at points subjected to great stresses. Fissures may in extreme cases be formed, but these will once more become frozen up if the sides are pressed together. Sometimes two tributary glaciers meet each other at some point in their courses, and proceed afterwards as a single glacier, both becoming frozen together, a track of stones and *débris* alone marking the line of separation of the two streams of ice.

2. According to Professor Forbes, we must consider ice to partake somewhat of the properties of a plastic solid. Every one has seen candles which have become considerably bent under their own weight, especially in warm weather, although melting has not occurred. Sticks of sealing wax will bend in a similar manner. A long bar of ice when supported at its ends and weighted near its centre will also become bent. According to Professor Forbes, the motion of a glacier differs only in degree from that of a stream of treacle running down an incline.

3. Canon Moseley attributes glacier motion to temperature variations. Thus, when ice below 0° C. is heated, it expands; it will naturally expand so that its lowest part moves downwards, since an upward motion would necessitate the lifting of great masses of ice in opposition to the force of gravity. On the other hand, when cooling takes place, a contraction will occur, and the higher portions of the glacier will be pulled downwards. Thus a glacier gradually creeps downwards, just as sheets of lead on slanting roofs have been observed to do. The upper surface of the glacier being heated most, will move the fastest.

According to Koch and Klocke, glaciers move steadily downwards during the afternoon, a slight backward motion occurring at night. In the morning hours the motion is irregular.

There seems little reason to suppose that the actions contemplated in the above three theories do not take place simultaneously. The extent to which any one cause is operative will of course vary for different glaciers, and even for different parts of the same glacier. Thus, cases are known where a glacier falls over a precipice; the ice breaks away above and recombines below. Here regelation is unquestionably the chief agent. On the other hand, the motions observed by Koch and Klocke can hardly result from anything but temperature changes.

EVAPORATION.

Evaporation.—It may here be worth while to anticipate to a small extent the principles detailed in the chapter devoted to the kinetic theory (Chap. XIII). Chemists have shown that we must consider all material substances to consist of molecules, each of which may comprise a number of atoms. According to the kinetic theory, these molecules are in rapid motion among themselves. In a solid it is probable that the molecules vibrate about a constant mean position. In liquids a molecule can move from any one position to any other, being hindered only by the frequent collisions with other molecules which occur. In a gas, the molecules being much more sparsely scattered, fewer collisions occur, and consequently a molecule will move from one position to another in much less time.

In the case of a liquid, the molecules are so close to each other that considerable forces are exerted between them. A molecule in the middle of a quantity of liquid will on the average be pulled in all directions simultaneously to about an equal extent. When, however, a molecule is situated near the surface of a liquid, the number of molecules pulling it back into the liquid will exceed those pulling it toward the surface. Consequently the surface of a liquid will be drawn inwards, and will for this reason act somewhat like an elastic membrane. This accounts for the fact that a drop of water can hang on the under side of a horizontal plate of glass without falling to the earth.

This straining action exerted on the surface of a liquid, and tending to reduce its area, is termed the *surface tension* of the liquid.

It has been found possible to explain the greater number of the phenomena connected with heat, by supposing that the molecules of a body are in more violent agitation when the body is hot than when it is cold. Indeed, the *heat* contained by a body is considered to be merely the kinetic energy of its constituent molecules.

We are at liberty to consider that in a liquid at a constant temperature, a molecule may be moving with greater velocity at one moment than at another, and therefore, that at any instant some molecules are moving more rapidly than the rest. A molecule moving with great velocity might escape from the surface of a liquid, even though the greater number of molecules near it were pulled back into the liquid as previously described. If the temperature of the liquid is high enough, most of the molecules near the surface can readily escape; the liquid is then at its boiling point, and evaporation takes place freely. But evaporation may take place at much lower temperatures, as is proved by the fact that in countries where snow lies long on the ground, the whole of a fall of snow may gradually disappear without the temperature rising above 0° C. In this and similar cases the molecules which escape are those possessing at the instant the greatest velocity perpendicular to the surface.

Vapour.—The molecules which have escaped from the surface of the liquid, thenceforth exist in a state somewhat similar to that pertaining to the molecules of a gas. When, however, a substance can exist in a gas-like and liquid state at the same temperature, the term *vapour* is applied to the aggregate of the molecules in the free or gas-like condition. The distinction between vapours and gases will be further dealt with in the next chapter.

If evaporation takes place into a closed space, some of the molecules of the vapour, after wandering about for a time, will strike on the surface of the liquid, and be again drawn into it. Other molecules will, however, be escaping, and it is clear that after a certain time a state of equilibrium will be reached, in which as many molecules return to the liquid in a second as leave it in that time. The vapour is then said to be in a *saturated* condition.

When, however, a saucer full of water is placed in an open room, the vapour which leaves the surface of the water is hardly likely to return to it. If the air in the room is not saturated with water vapour, more molecules will leave the water than return to it from the atmosphere. In this case evaporation will continue till the water has disappeared.

Mist.—Some vapours, such as those of iodine and bromine, as well as the gas chlorine, are coloured; but the vapour of a colourless liquid is generally transparent. Thus, steam is transparent, as may be seen by examining the space above boiling water in a glass flask. When steam is condensed into a number of very small drops of water, a cloud or mist is formed. It is really a mist, or a collection of finely divided water drops, that is seen issuing from the spout of a kettle. The condensation of steam or vapour of water into mist has been found by Aitken to depend on the presence of fine particles of dust in the atmosphere. More recently Mr. C. T. R. Wilson has found that a ray of ultra-violet light will condense saturated water vapour to mist.

Cold produced by Evaporation.—Since the molecules which leave a liquid during evaporation are moving with more than the average velocity of the remaining molecules, the energy of the latter will decrease with every molecule that escapes. In other words, the water left in the saucer will become continually colder, unless heat is communicated from external sources.

EXPT. 48.—Place some water in a shallow dish, and support this above a larger dish containing strong sulphuric acid, the whole being placed under the receiver of an air pump. On exhausting the receiver, evaporation will take place rapidly from the water, the vapour being continuously absorbed by the sulphuric acid. When the pressure has been sufficiently reduced the water will commence to boil, losing heat so rapidly thereby that the remainder shortly afterwards becomes frozen.

EXPT. 49.—Place some ether in a beaker, and stand this on a piece of wood on which a pool of water has been collected. Blow air through a glass tube, the end of which dips below the surface of the ether. By this means rapid evaporation of the ether is facilitated. The cold produced will freeze the water below the beaker.

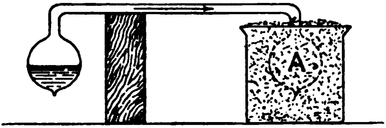

FIG. 82.—Wollaston's cryophorus.

Wollaston's Cryophorus.—This is a piece of apparatus consisting of two bulbs (Fig. 82) connected by a tube. One of the bulbs contains water, the remainder of the space enclosed in the apparatus being freed from air. If the bulb A be placed in a mixture of ice and salt, the extreme cold will condense the vapour contained in it. More vapour will leave the water in the other bulb, to be condensed in its turn. The cold produced by the continual evaporation will finally freeze the remaining water.

Carré's Freezing Machine.—This is constructed so that the space above the water contained in a flask C (Fig. 83) can be exhausted of air by a pump A, whilst the aqueous vapour which is given off is absorbed in a vessel B, containing strong sulphuric acid. The walls of the vessel are made of an alloy of antimony and tin which is not attacked by the acid.

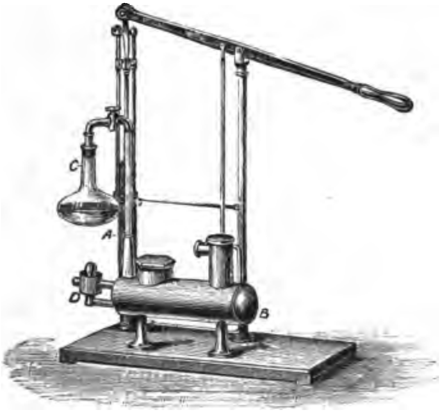

FIG. 83.—Carré's freezing machine.

In another form of freezing apparatus, also invented by Carré, an aqueous solution of ammonia is first heated to about 130° C. in a strong iron vessel A, Fig. 84, the ammonia which is expelled being condensed in the space between the double walls of the vessel D, which is surrounded with water. When sufficient ammonia has been distilled over in this manner, the vessel A is cooled by being surrounded with water. The ammonia evaporates from the vessel D, which consequently falls in temperature, water which has been previously placed in E, the central compartment of D, being thereby frozen.

In the large towns of the southern states of North America, where ice is almost a necessity of daily use, pipes supplying liquid ammonia, and others through which the vapour can return to a central cooling apparatus, are laid on to the houses.

At Niagara in London, ice for skating is produced throughout the year by causing strong brine, which has been cooled in an apparatus similar to that just described, to circulate through pipes which traverse a shallow basin initially filled with water.

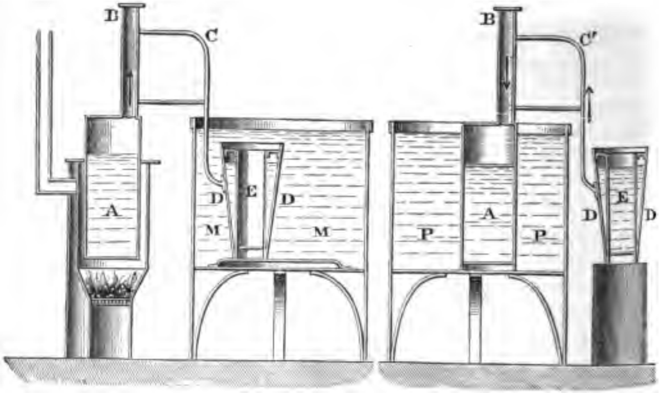

FIG. 84.—Carré's system of refrigeration by the evaporation of liquid ammonia. (P).

EBULLITION OR BOILING

EXPT. 50.—Take a flask containing about 50 c.cs., clean it with strong sulphuric acid, and then half fill it with water, and place it on a sand bath above a Bunsen burner. Note the changes which take place in the water in the flask. They will be somewhat as follows:

1. Small bubbles will be formed on the inside of the walls of the flask, growing larger by degrees, and finally ascending to the surface of the water. These are bubbles of air driven out of solution by heating.

2. Bubbles will commence to form, probably at some particular point of the bottom of the flask, and will rise towards the surface of the water, collapsing with sharp clicks before reaching it. These are bubbles of steam condensed by the water which has not everywhere reached the boiling point.

3. After a time the bubbles cease to collapse in the water, but burst on the surface. The water is now boiling, or is in a state of ebullition.

Continue the heating for some time. It may happen that the bubbles no longer stream off from a particular point, but that ebullition occasionally ceases for several seconds, a large volume of steam being then suddenly formed, which throws the water violently upward in the vessel. This phenomenon is termed *bumping*. Place a thermometer so that its bulb dips into the liquid. Notice the temperature indicated when the water is boiling by bumping. Then lower a small fragment of coke or broken flower pot, attached to a piece of cotton, into the water. Notice that bubbles of steam are at once given off from this piece of coke or porous earthenware, and that bumping ceases. Your thermometer will probably indicate that the temperature of the water has fallen.

In the case of a liquid to which heat is continuously communicated, in order that a stationary temperature (termed the boiling point of the liquid) should be attained, heat must, as fast as it is communicated, be absorbed or rendered latent in the conversion of the liquid into vapour. When no bubbles of vapour are formed in the interior of the liquid, vaporisation can only take place at the free surface. The temperature of the main bulk of the liquid may therefore rise considerably above its boiling point.

The way in which porous substances act in promoting the free evolution of vapour is not exactly known. It would at first sight appear probable that the action is due to air contained in the cavities of the substance, the more so, as small pieces of fine capillary tube exercise a similar influence. According to this theory, the molecules of the liquid escape into the small volume of air just as those near the free surface escape into the atmosphere. Mr. Charles Tomlinson has shown, however, that a fine wire gauze cage filled with air could be lowered into superheated water without ebullition occurring. On the other hand, water, which was heated above its normal boiling point, was thrown into violent ebullition when its surface was touched by a slip of paper, a piece of wire, or the end of a glass rod. When a glass rod was entirely immersed in it, steam was at first given off from the whole of its surface, but after a time only a couple of minute specks in the glass remained active. A piece of flint immersed in the liquid was active over its entire surface, but on being broken in two no steam was given off from the freshly formed surfaces. A rat-tailed file, which at first was extremely active in promoting ebullition, was rendered inactive by being heated in a spirit lamp and cooled in the vapour above the liquid.

The conclusion arrived at by Mr. Tomlinson was, that the activity of a surface in promoting ebullition is proportional to its want of chemical cleanness. Thus, the freshly formed surfaces of the broken flint were chemically clean, whilst those which had been for a long time in contact with the atmosphere were chemically dirty. This explanation, when carefully considered, is not quite as definite as it appears at first sight. Chemically, dirt is matter in the wrong place, *i.e.*, matter where we don't want it. According to Mr. Tomlinson, a rod of metal with a clean surface would be inactive in producing ebullition; on the other hand, a trace of that metal obtained by rubbing the rod on the clean surface of a broken flint would constitute chemical dirt, and ought to promote ebullition. It is known that substances like glass condense on their surfaces layers of gas. Perhaps it is this layer which is active in promoting ebullition.

If a glass of fresh soda-water be examined, it will be found that bubbles of gas are given off from small points on the surface of the glass. A piece of porous earthenware, or a lump of sugar, will be found to promote the evolution of the gas.

Experimental Determination of Boiling Points.—From what has previously been said, it appears that the temperature of a liquid may, in certain circumstances, rise considerably above its normal boiling point. Consequently it is only in determining the boiling points of solutions that the thermometer is placed in the liquid, and some arrangement must then be made to promote free ebullition.

The usual method of determining the boiling point of a pure liquid is to place the bulb of the thermometer in the vapour given off during ebullition. The space containing the thermometer should be jacketed in the manner described in connection with the determination of the boiling point of a thermometer (p. 11).

The actual temperature of the vapour above a boiling solution is generally slightly lower than the temperature of the solution. Thus above a salt solution, the temperature of which is 110° C., the steam may reach a temperature, say, of 105° C. A thermometer placed in this steam will, however, indicate a temperature of 100° C. The reason of this is, that the steam condenses to pure water on the bulb and stem of the thermometer, and as this water has a large surface, any further heat communicated will cause part of the water to evaporate without a rise of temperature occurring.

On the other hand, if the temperature of the thermometer falls below 100° C., steam will be condensed on it, and the temperature will be raised by the latent heat rendered up.

In order to provide a larger surface for evaporation, the bulb of the thermometer is often surrounded loosely with cotton wool.

Determination of the Boiling Point of a Solution.—As pointed out above, a thermometer when placed in the steam given off from a boiling aqueous solution of a salt, will indicate the boiling point of the water, and not that of the solution. A similar law applies to solutions in general.

In order to determine the boiling point of a solution, the thermometer bulb must be completely immersed. Special precautions must be taken to prevent the occurrence of boiling by bumping, and the consequent rise of temperature of the solution above its boiling point.

Beckmann's Boiling Point Apparatus.—Fig. 85 represents diagrammatically the essential points of Beckmann's apparatus for determining the boiling points of solutions. A test tube A, provided with a side inlet tube B, is used to contain the solution. A piece of platinum wire P, is fused through the bottom of the test tube, and a number of glass beads, G, are also contained by it. The beads and platinum wire serve to promote free ebullition. The bulb of a sensitive thermometer T, similar to that described on p. 15, dips into the solution. A spiral glass tube, K_1, serves to condense the vapour given off; the condensed liquid runs back into the solution, so that the strength of the latter is maintained constant.

The test tube containing the solution is surrounded by a glass vessel C, provided with double walls, forming a vapour jacket. A liquid, possessing a boiling point slightly higher than that of the solution in A, is placed in C; some pieces of porous earthenware, D, serve to promote free ebullition, whilst the condensing spiral K_2, prevents loss of the liquid.

The whole of the above arrangement is mounted on a stand made from asbestos mill-board. Two pointed Bunsen flames play on the wire gauze E, and the hot gases impinge directly on the lower surface of the vapour jacket C. Direct communication of heat to the vessel, A, is prevented by the double cylinder, F_1, F_2, of asbestos mill-board, and by a roll, H, of asbestos paper. Thus the solution in A receives heat only from the liquid and vapour in the vessel C.

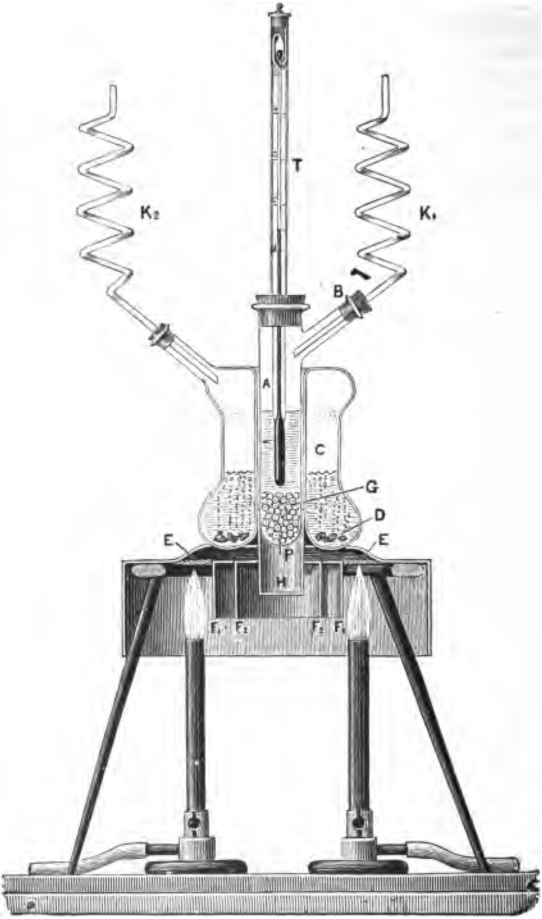

FIG. 85.—Beckmann's boiling point apparatus.

The solution may be introduced into the vessel A by way of the side inlet tube B, the condenser K_1 being removed.

A Solution of a Non-volatile Substance will possess a higher Boiling Point than that of the pure Solvent.—The following table, taken from Lupke's *Electro-Chemistry*, exhibits the elevation of the boiling point produced by dissolving definite quantities of cane sugar in water.

Mass of cane sugar dissolved in 100 grms. of water.	Barometric pressure.	Boiling point of water.	Boiling point of solution.	Elevation of boiling point.	Elevation of boiling point per gram of dissolved sugar.	Molecular elevation of boiling point.
34·2 grms.	746 mm.	99·85° C.	100·35°C.	0·50° C.	·0146° C.	5·00° C.
51·3 ,,	746 ,,	99.85	100·59	0·74	·0144	4·93
68·4 ,,	755 ,,	99·90	100·95	1·05	·0153	5·24
85·5 ,,	755 ,,	99·90	101·22	1·32	·0154	5·28

From this table it is evident that the elevation of the boiling point is approximately proportional to the mass of the substance dissolved.

The molecular elevation of the boiling point is obtained by multiplying the elevation, per gram of the dissolved substance, by the molecular weight of the latter. If various substances are used, the molecular elevations will denote the elevations produced by dissolving equal numbers of molecules of the various substances in equal masses of water.

It has been found that for substances which form electrical non-conducting or badly-conducting solutions in water, the molecular elevation of the boiling point has a constant value of about 5. Thus *solutions comprising equal numbers of dissolved molecules in equal masses of water possess the same boiling point.*

In the case of aqueous solutions of substances such as sodium chloride, which are good conductors of electricity, the molecular elevation of the boiling point amounts to nearly 10. This is in agreement with the theory, mentioned on p. 170, that such substances are dissociated into simpler elements when dissolved in water.

Variation of the Boiling Point with Pressure.—The volume occupied by a given mass of any substance is always much greater in the state of vapour than in that of liquid. In other words, a considerable expansion takes place during the vaporisation of a liquid. Thus 1 gram of water at 100° C. occupies a volume of 1·043 c.cs. When converted into steam at 100° C., the volume occupied at normal atmospheric pressure will be about 1650 c.cs.

It is obvious that an increased pressure will tend to hinder this expansion, and therefore to prevent the conversion of water into steam. Hence a higher temperature is required to convert water into steam at a high pressure than would suffice at a low pressure.

EXPT. 51.—Take a round-bottomed flask of about 300 c.cs. capacity, half fill it with water, and boil it for a few minutes over a Bunsen flame. When steam has been given off for a sufficient time for you to feel satisfied that the air in the flask has been expelled, remove the burner, and the instant ebullition ceases, close the mouth of the flask with a well-fitting indiarubber stopper. Invert the flask, and cool it by squeezing cold water on the bottom of it (Fig. 86). You will find that ebullition recommences, and can be produced even when the water has cooled very considerably.

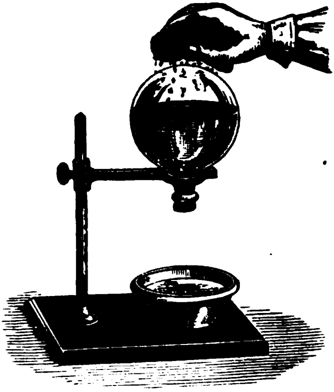

FIG. 86.—Water boiling under diminished pressure.

In this experiment the pressure of the steam or water vapour, at the instant of closing the mouth of the flask, was equal to the atmospheric pressure. On subsequently cooling the bottom of the flask, part of this vapour is condensed, so that the remainder exerts a pressure less than that of the atmosphere. Ebullition recommences because less hindrance is given to the formation of vapour.

As this point is one of some importance, the following explanation, couched in terms of the kinetic theory, should be carefully followed.

At the instant when the flask is closed, the number of molecules returning into the liquid in a given time is just equal to the number leaving its surface in that time. On cooling the bottom of the flask, the total number of molecules in the state of vapour is enormously decreased, so that fewer have an opportunity of re-entering the liquid. Consequently the number of molecules leaving the liquid is greatly in excess of the number returning to it, thus giving rise to the appearance of ebullition.

In the manufacture of sugar, the aqueous solutions are concentrated by boiling under diminished pressure, the necessary temperature being thus reduced, and charring of the sugar avoided.

A table giving the boiling point of water for various pressures is given on p. 27. Additional information will be found in Chap. XVI.

The Hypsometer.—During the ascent of a mountain the limits of the atmosphere are continually approached as greater and greater altitudes are reached. The atmospheric pressure at any place is equal to the weight of the air contained in an imaginary tube of unit sectional area, extending vertically from the place in question to the furthest limits of the atmosphere. Hence it is evident that the barometric pressure falls as we ascend to greater altitudes.

When the pressure at any stage of a mountain ascent has been obtained, the height of the station above the sea level may be calculated, or obtained by reference to tables.

A barometer may be used to determine the required pressure. But as mercury barometers are somewhat cumbersome, and other barometers are not always to be depended upon, it is usual to employ other means for determining the pressure.

The temperature at which water boils is, as we have seen, related to the pressure to which its vapour is subjected. Hence an observation of the boiling point of water may be used to determine the barometric pressure, and from that the height of the station above the sea level.

The instrument used for determining the boiling point of water, in order to determine the altitude of a station, is called a Hypsometer. Fig. 87 shows such an instrument (made by Messrs. Yeates and Sons of Dublin), as a whole and in parts.

Water is contained in a metal vessel C. This is provided with bent metal tubes D, communicating with its interior. A lamp A is screened from draughts by a case B; the flame plays on the tubes just mentioned. The hot gases generated by combustion escape into the open air through oblique tubes E which pass through the water.

The steam generated passes upwards through the inner of two concentric metal tubes F, and thence into the space between the tubes by way of some holes, H, and finally escapes into the atmosphere by an aperture G. Thus the steam in the central tube is protected from loss of heat by means of a steam jacket.

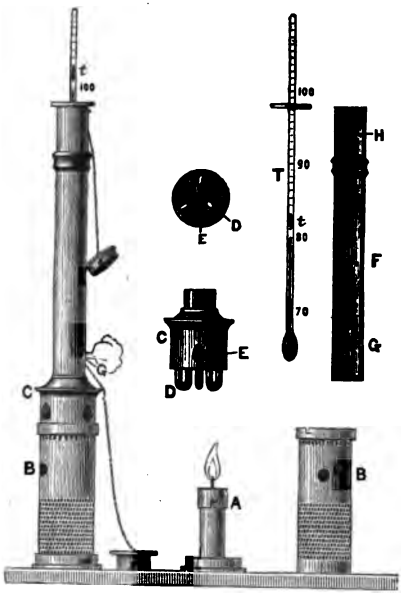

FIG. 87.—Hypsometer.

The thermometer T is provided with a small thread of mercury *t*, which is separated from the main column by a small bubble of air. When the thermometer is heated, the main column of mercury pushes this thread before it, but when it is cooled, the thread maintains its position, thus indicating the highest temperature attained.

In making an observation, the thread of mercury is shaken down as near to the bulb as it will go, and the thermometer is then placed in the central tube of F, and the water is boiled. If the extremity of the mercury column is visible at the top of the instrument, an observation may be made directly; if not, the thermometer must be removed, and the position of the detached thread noted.

Boiling under increased Pressure.—At great altitudes where water boils at very low temperatures, some contrivance must be used in order to attain a sufficiently high temperature to cook food. This is generally managed by using a strong vessel provided with a safety valve which only allows the steam to escape when a sufficiently high pressure has been reached. Thus, if water is required to boil at 100° C., it is arranged that the pressure per square inch necessary to raise the valve, added to the atmospheric pressure per square inch, should amount to 15 lbs.

The boiling point of water may, when necessary, be raised to a considerable extent by similar means. Fig. 88 represents Papin's digester. The lid of a strong metal vessel is held in position by a screw, and a valve is closed by means of a lever carrying a movable weight. Water may be caused to boil at 200° C. by subjecting its vapour to a pressure of 240 lbs. to the square inch, *i.e.*, to a pressure of 16 atmospheres.

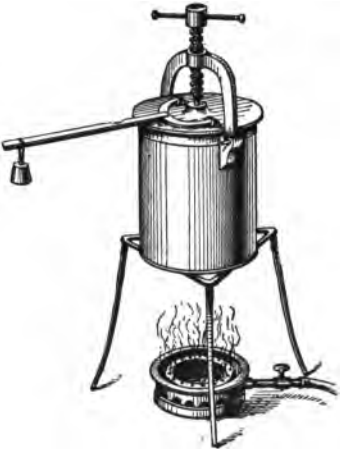

FIG. 88.—Papin's Digester.

The Spheroidal State.—

EXPT. 52.—Take a flat piece of sheet copper or brass, and support this, in a horizontal position, over a Bunsen burner. From time to time, whilst the plate is being heated, allow a few drops of water to fall on it from a pipette. When the plate is quite cool, the water will spread over it in the usual way. As its temperature increases, an accelerated rate of evaporation will be noticed, and when a certain temperature has been attained, violent ebullition will ensue. On still further heating the plate, a stage will be reached where the water, instead of spreading over the surface, or being thrown into ebullition, collects itself in small spheroidal drops, which run over the surface very much as mercury does when spilt on a table. If the plate is horizontal, one of these drops may be observed for a considerable

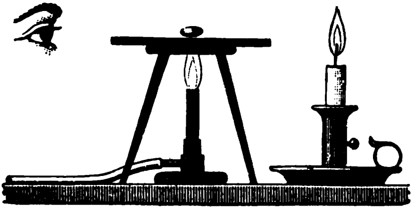

FIG. 89.—Drop of water in the spheroidal state.

time, and it will be found that its size decreases very slowly. If a luminous flame is placed in a suitable position, so that it is seen behind the drop by an eye placed on a level with the plate, it will be noticed that the drop does not touch the plate. It is, in fact, supported by a cushion of steam. The escape of the steam from under the drop often throws the surface of the liquid into beautiful undulations.

EXPT. 53.—Make a borax bead on the end of a fine platinum wire, and having heated this to as high a temperature as possible in a Bunsen flame, quickly immerse it below the surface of some water in a beaker. It will be observed that there is at first a shell of vapour surrounding the bead, which prevents the water from coming in contact with it. When the bead has cooled to a certain temperature, the water suddenly gains access to it, as is denoted by the disappearance of the shell of vapour, and the production of the characteristic hissing sound.

The above experiments illustrate what is termed the spheroidal state of water. A laundress generally tests the temperature of her iron by observing whether it is sufficient to cause a drop of saliva to assume the spheroidal state. Jugglers were formerly in the habit of plunging their hands into molten lead, their immunity from burning depending on the moisture on their hands assuming the spheroidal state. Blacksmiths will often lick a bar of red-hot iron. In early times, a common form of ordeal was to walk on red-hot ploughshares; many who came through this ordeal triumphantly must have ascribed to supernatural intervention an occurrence which was strictly in accordance with natural law.

Water is not the only substance which can assume the spheroidal state. All liquids will do so if placed on a metal surface that is sufficiently hot. If a mixture of solid carbonic acid and ether is poured into a red-hot platinum crucible it will assume the spheroidal state. If mercury is poured on to the mixture, it will be frozen, though the platinum dish remains red-hot.

Sublimation.—In certain cases a solid may change directly into a vapour without undergoing liquefaction. A familiar instance is afforded by iodine. This process is termed sublimation. Its reverse (*i.e.*, direct passage from the state of vapour to that of solid) occurs in the formation of hoar frost.

The conditions which determine whether sublimation or liquefaction will take place may be easily understood. If the vapour pressure of a solid at any temperature is greater than one atmosphere, the substance will pass directly from the solid to the vaporous condition. By increasing the pressure, however, the substance can be obtained in the liquid state, provided that the change from liquid to solid is accompanied by an expansion. Thus arsenic, which sublimes under ordinary pressures, may be liquefied if the pressure is sufficiently increased.

(See, also, the discussion of the triple point curves, p. 233.)

SUMMARY.

Cooling Curves.—When a pure liquid is cooled, the temperature falls in a regular manner until solidification commences. The temperature then remains constant until the whole of the substance has become solidified, when a further regular fall of temperature occurs.

Over Cooling.—When a liquid is cooled gradually, and is protected from dust and mechanical disturbances, its temperature can be reduced considerably below its freezing point without the occurrence of solidification. On introducing a fragment of the solid substance, or on stirring the liquid violently, solidification commences, and the temperature rises to the melting point of the substance.

The Freezing Point of a Solution is always lower than that of the pure solvent. Equal numbers of molecules of various substances dissolved in equal masses of the same pure solvent, produce equal depression of the freezing point. Substances which, when dissolved in water, produce electrically conducting solutions, appear to be dissociated.

The Solution of Crystalline Substances is generally accompanied by a fall of temperature.

Change of Volume on Solidification.—Water and several other substances expand when solidified. 10 c.cs. of water at 0° C. form about 11 c.cs. of ice at the same temperature. When ice is cooled, it contracts.

In Bunsen's Ice Calorimeter quantities of heat are measured by observing the alteration of volume of a mixture of ice and water at 0° C.

Effect of Pressure on Melting Point.—When a substance which expands on solidifying is subjected to a high pressure, the melting point is lowered. The melting point of a substance which contracts on solidifying is raised in similar circumstances.

Regelation.—Two pieces of ice can be frozen on to each other by pressing them together. The ice is melted at the point of contact by the pressure to which it is subjected, and freezing occurs when the pressure is released.

A Glacier is a river of ice formed from compressed snow. The motion of a glacier is rendered possible partly by regelation and partly by the plasticity of ice. Expansions and contractions of the ice under changes of temperature also produce important effects.

Vapour.—When a substance existing in a gas-like condition can be converted into a liquid by increased pressure without any change of temperature, the substance is said to be in a state of vapour.

Evaporation consists in the quiet conversion of a liquid into a vapour.

Cold produced by Evaporation.—When a liquid is caused to evaporate quickly, under such conditions that no heat is communicated to it, the remaining liquid is cooled.

Ebullition or Boiling.—When a liquid is converted into a vapour under such conditions that bubbles of the vapour are formed in its interior, the liquid is said to boil, and the process is termed ebullition. Under a given pressure a liquid boils at a constant temperature if small pieces of porous earthenware, capillary tube, &c., are placed in it.

The Boiling Point of a Solution of a non-volatile substance is always higher than that of the pure solvent. In a dilute solution the elevation of the boiling point is proportional to the number of molecules dissolved in a given mass of the pure solvent. Substances which form electrically conducting solutions are apparently dissociated into simpler elements during solution.

The Boiling Point of a Liquid is always raised by an increase of pressure. Water may be caused to boil at 200° C. by subjecting it to a pressure of 16 atmospheres.

The Hypsometer is an instrument for determining the barometric pressure from the boiling point of water. It is used in determining the heights of mountains.

Spheroidal State.—When a drop of a liquid is placed on a metallic surface heated to a sufficient temperature, it collects itself into a spheroidal globule separated from the surface by a cushion of its own vapour.

Sublimation.—This term is applied to the direct passage from the solid to the vaporous state. Substances which sublime at ordinary pressures may be caused to melt by the application of a sufficiently high pressure.

QUESTIONS ON CHAPTER VIII.

(1) Describe an experiment to show that water can be frozen by its own evaporation. Under what circumstances may the freezing point of water and its boiling point coincide. Discuss the consequences of such an arrangement.

(2) Explain the method of using Bunsen's ice calorimeter to determine specific heats.

(3) Discuss the evidence that solids can evaporate, and that vapours can be deposited as solids without passing through the liquid state.

(4) How does a change of pressure affect the temperature of the freezing point of water?

How is this change explained on the principles of the mechanical theory of heat?

(5) Twenty-five grams of water at 15° C. are put into the tube of a Bunsen ice calorimeter, and it is observed that the mercury moves through 29 centimetres. Fifteen grams of a metal at 100° C. are then placed in the water and the mercury moves through 12 centimetres. Find the specific heat of the metal.

(6) Describe and explain the spheroidal state of a liquid.

(7) Describe the phenomena observed during the fusion or solidification of an alloy of two metals, and give some explanation of the phenomena.

(8) Explain in what way the melting points of bodies are affected by pressure. Illustrate your answer by reference to the case of water and wax.

(9) Explain exactly the adhesion of two pieces of ice when pressed together at the melting point and then released. Calculate the effect of an extra atmosphere of pressure on the melting point of a substance which contracts on solidifying by one-sixth of its volume in the liquid state, whose latent heat is 40 units, whose ordinary freezing point is 27° C., and whose specific gravity when liquid at this temperature is 1·2. (For answer to last part of this question, *see* Chap. XVII.)

(10) Define the boiling point of a liquid. Describe carefully the various conditions which influence it.

(11) Explain Bottomley's experiment in which a loaded wire cuts its way through a block of ice and leaves the block whole after its passage. Why is it that the wire always tends towards a circular curvature?

(12) Describe how to use Bunsen's ice calorimeter.

(13) A water-bottle is covered with felt; explain why the contained liquid may be cooled by moistening the felt, and placing the bottle in a dry room.

(14) Heat is continuously applied to a mass of ice at 10° C. until it becomes steam at 100° C. Trace as completely as you can the change in volume and temperature that takes place.

(15) Describe carefully the process of ebullition, and give reasons why a change of external pressure has an effect on the boiling point.

Why is the boiling point on a thermometer determined by immersing the instrument in the steam from boiling water?

(16) Give physical reasons why (*a*) glass cracks when suddenly heated; (*b*) water thrown on a red-hot surface does not boil.

Explain the formation of hoar-frost, and the phenomenon of regelation.

(17) Describe carefully the difference between evaporation and boiling. What effect has the presence of air above the liquid on each? Why does ether boil at a lower temperature than water?

(18) Describe the phenomenon of boiling. How would you show that at the boiling point the vapour tension of a liquid equals the atmospheric pressure, and how do you suppose that boiling results from this equality?

PRACTICAL.

(1) Make a table of boiling points of a given salt solution.

CHAPTER IX

CONTINUITY OF STATE

Boyle's Law at High Pressures.—The construction and use of a piece of apparatus designed to determine the relation between the pressure and the volume of a certain quantity of gas, the pressure varying between 1 and about 3 atmospheres, has already been described (p. 90). The student who has carefully performed the experiment as stated, and has reflected on the results obtained, will probably have noticed a very serious defect in the process. The aim of a careful experimenter should be to attain as uniform an accuracy as possible throughout an experiment. In the experiment in question, the pressures can be measured with sufficient accuracy throughout; but the accuracy with which the volumes occupied by the gas can be determined decreases as the pressures are increased.

Thus, let us suppose that the gas occupied a volume of 100 c.cs. at atmospheric pressure, and that the possible error in estimating the position of the mercury meniscus may lead to an error in the determination of the volume amounting to ·1 c.c. Then the *percentage error* in determining the volume will be ·1.

At two atmospheres pressure, the volume will be approximately halved, and as a mistake in reading, involving an error of ·1 c.c. in the observed volume, may still be made, the percentage error will amount to ·2 per cent.

Similarly, at three atmospheres pressure, a mistake amounting to ·3 per cent. of the total volume may be made. If it were possible to increase the pressure to 100 atmospheres, the possible error would amount to 10 per cent. of the volume of the gas at that pressure.

Hence, experiments on the relation between the pressure and volume of a gas, conducted by the method described, become inaccurate just at the point where accuracy is most desirable.

Regnault's Experiments.—The arrangement used by Regnault to overcome the difficulties indicated above may be understood from Fig. 90.

A certain quantity of a gas in a pure and dry state was enclosed in a strong glass tube AB. The lower end of this tube contained mercury, and was connected by means of a tube BC with a long manometer tube CD, open at the top; and also with a pump, by means of which more mercury could be introduced. The temperature of the air in AB was maintained constant by means of a water jacket

At the commencement of an experiment, the mercury surfaces in AB and CD were adjusted to be in the same horizontal plane, and the barometer was read. Mercury was then pumped in through EC till the gas in AB occupied only half of its initial volume. The difference in the heights of the mercury surfaces in AB and CD was then observed, and this difference, added to the barometric pressure, gave the pressure to which the gas was subjected.

The stop-cock T was then opened, and gas was pumped into AB till a volume equal to the initial one was enclosed under a pressure of two atmospheres. The stop-cock T having been closed, and the relative positions of the mercury surfaces observed, mercury was again pumped in until the volume of the enclosed gas was

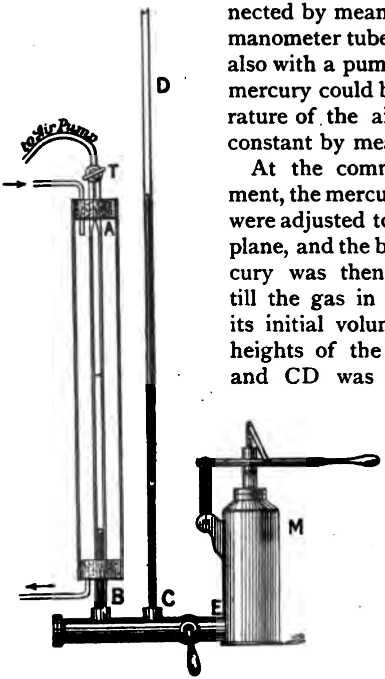

FIG. 90.—Regnault's apparatus for investigating the truth of Boyle's Law at high pressures.

halved. Similar observations to those already described were made, and the above operations were repeated until a pressure of between 14 and 15 atmospheres was reached.

Regnault thus found that no gas accurately obeys Boyle's Law. For most gases he found the product pv decreased as p increased, leading to the conclusion that a given increase of pressure produced a greater diminution of volume when the initial pressure was high, than it did when the pressure was low. For hydrogen, however, the product of pv was found to increase with p.

Amagat's Experiments.—Amagat has investigated the behaviour of gases at very high pressures. Nitrogen was first examined by a method somewhat similar to that used by Regnault, but an open air manometer tube 65 metres (about 213 ft.) in height was used. The behaviour of other gases was then compared with that of nitrogen, by enclosing equal volumes of nitrogen and the gas in question in similar tubes, and then subjecting both to the same pressures.

Figs. 91 and 92 exhibit the relation between the product pv and the pressure p for hydrogen and nitrogen, at several temperatures between 17° C. and 100° C. It will be noticed that in the case of hydrogen, the product pv increases throughout with the pressure. In the case of nitrogen, the product pv at first diminishes, and subsequently increases, as the pressure is increased.

Fig. 93 exhibits the relation between the product pv and the pressure p in the case of carbon-dioxide. The curves referring to high temperatures resemble those for nitrogen, but at low temperatures the minimum points on the curves are greatly exaggerated. It may be noticed that in the case of nitrogen and the high temperature curves for carbon-dioxide, the lowest parts of the curves are nearly parallel to the axis of pressures. In these neighbourhoods therefore the product pv is constant.

Andrews's Experiments.—The experiments of Amagat which have just been described were undertaken about 1870. As early as 1863, Dr. Andrews performed a classical series of experiments which led to a clear comprehension of many phenomena which up to then had received only very partial explanations.

The gas which he experimented with was carbon-dioxide, the pressures being determined by observing the compression of a certain quantity of atmospheric air.

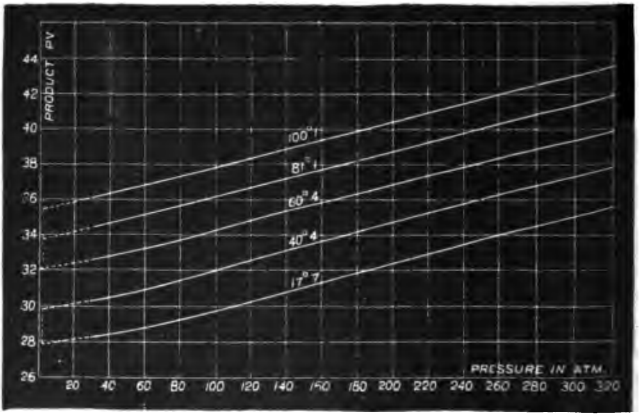

FIG. 91.—Amagat's curves for hydrogen. (P.)

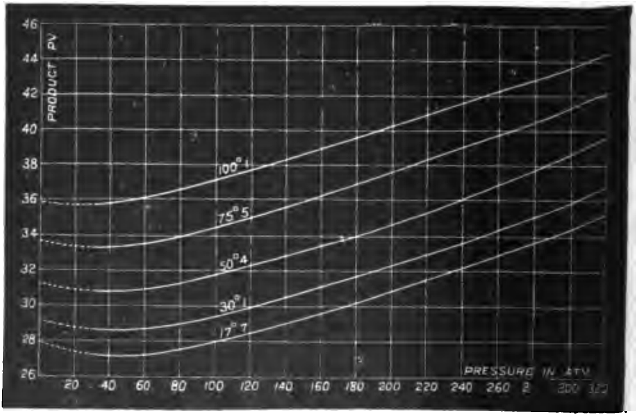

FIG. 92.—Amagat's curves for nitrogen. (P.)

Two tubes similar to that represented in Fig. 94 were employed, carbon-dioxide being enclosed in one and atmospheric air in the other. Each of these tubes comprised a rather wide part AB, to the end of which a piece, BC, of thick walled tube with a fine bore was fused. This latter tube was carefully calibrated, so that the volume enclosed by 1 cm. length at any position was accurately known. In filling one of the tubes with carbon-dioxide, this gas was passed through it for a space of 24 hours; even then a small amount of air remained. The end C was then fused up, and the end D of the tube AD was placed below the surface of mercury and a small piston of mercury, E, drawn in by heating and subsequent cooling.

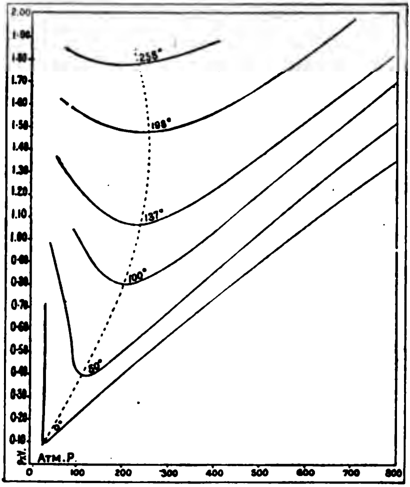

FIG. 93.—Amagat's curves for carbon-dioxide.

The end D was then placed below mercury, and the whole arrangement enclosed in the receiver of an air-pump. On partially exhausting, some of the contained gas escaped. Part of AB and the whole of AD became filled with mercury when the receiver was once more put in connection with the atmosphere.

The carbon-dioxide and air tubes were then firmly fixed in two strong copper cylinders, the part BC being left projecting in each case. Communication was established between the copper cylinders by means of a cross tube.

The cylinders were then filled with water, by means of which pressure could be transmitted from screw plungers to the enclosed gases. The volumes of the enclosed gases were determined from observations of the position of the mercury surfaces. Fig. 95 is a reproduction of a photograph taken from the actual apparatus used by Andrews, and now preserved in the Science Collection at the Albert and Victoria Museum, South Kensington.

The curves in Fig. 96 represent the *isothermals* of carbon-dioxide deduced from Andrews's experiments. As usual, volumes are measured horizontally to the right (as abscissæ), the corresponding pressures being plotted vertically (as ordinates).

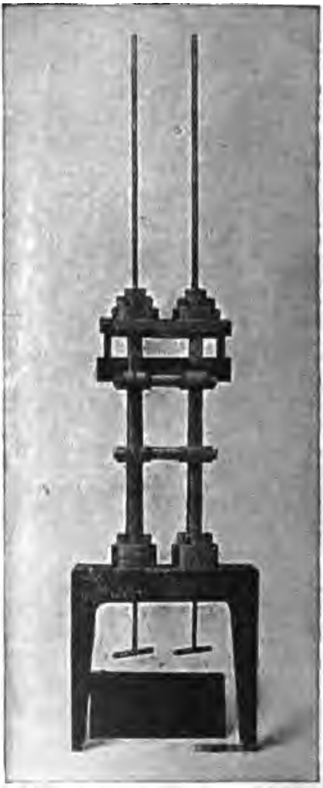

Fig. 95.—Andrews's apparatus for determining the isothermals of carbon-dioxide. (From a photograph.)

Let us examine the lowest of these curves, viz. the isothermal for carbon-dioxide at the temperature 13·1° C. Starting from the extreme right, we see that at first the volume of the CO_2 diminishes, as the pressure is increased, approximately in accordance with Boyle's Law. When, however, a pressure a little less than 50 atmospheres is reached, a discontinuity occurs, and the isothermal becomes horizontal. At this point Andrews observed that liquefaction commenced. As the volume was further diminished, a greater and greater proportion of the contained gas assumed the liquid form, *the pressure meanwhile remaining constant.* At the extreme left of this horizontal portion, all the gas had been converted into liquid; further increase of pressure produced only a very slight diminution in the volume occupied by the liquid, as is shown by the isothermal then becoming nearly vertical.

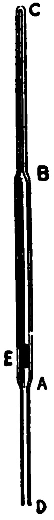

Fig. 94.—One of Andrews's experimental tubes.

The isothermal for 21·5° C. exhibits similar characteristics; it may be noted that liquefaction did not occur till a pressure of about 61 atmospheres was attained.

On now turning our attention to the isothermal for 31·1° C., it will be noticed that no sudden discontinuity can be traced. The conjecture that the abrupt discontinuities noticed in the isothermals for lower temperatures are associated with liquefaction of the gas was confirmed, since no formation of liquid could be observed at this temperature, even when the pressure was increased to 100 atmospheres.

It must be remembered that the only really essential difference between a liquid and a gas is that the former has a definite surface, exhibiting the ordinary curved form due to surface tension. No such surface could be noticed, however much the pressure was increased, when the temperature of the carbon-dioxide was at or above 31·1° C.

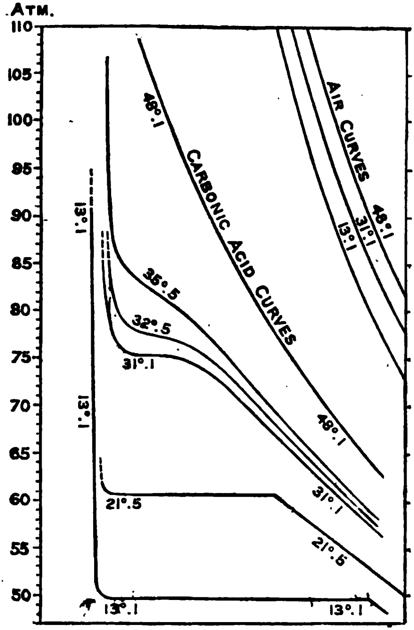

FIG. 96.—Isothermals of carbon-dioxide (Andrews).

Critical Temperature.—It follows from the above that at or above a temperature of 31·1° C. it is impossible to liquefy carbon-dioxide. At 30·92° C. and lower temperatures liquefaction could be effected. The latter is therefore termed the **critical temperature** of carbon-dioxide.

General Form of Isothermals.—The isothermals of a substance which cannot exist in a solid condition at ordinary pressures and temperatures, are represented in Fig. 97. The five lower isothermals all exhibit the discontinuity noticed by Andrews, which is associated with the passage of a part of the gas-like substance into the liquid state. In that part of the diagram shaded downwards from left to right, the substance is wholly in the liquid condition. In the cross-hatched space enclosed by the dotted curve, part of the liquid has been converted into the gas-like condition. Hence in this part of the diagram the substance exists in the state of a liquid in the presence of its saturated vapour. In that part of the diagram shaded downwards from right to left, the substance is in the state of unsaturated vapour.

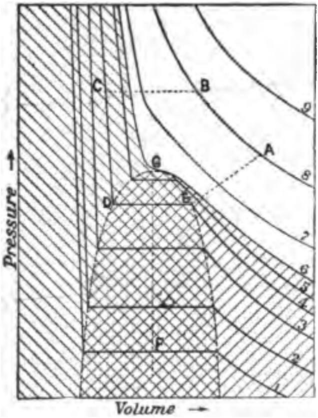

FIG. 97.—**Isothermals of a substance existing as liquid, vapour, and gas.**

The curve 6 is the isothermal for the critical temperature of the substance.

The curves 7, 8, 9 are isothermals for temperatures higher than the critical temperature. No liquefaction can take place at any point on these curves. In fact the substance is, at the temperatures corresponding to these curves, in the condition of a so-called permanent gas.

Some most important general conclusions may be drawn from a careful study of the curves given in Fig. 97. Thus, let us suppose that the point A on curve 8 corresponds to the volume and pressure of a certain quantity of gas at the atmospheric temperature. Let the pressure be increased, the temperature remaining unaltered, till the point B is reached; and then let the gas be cooled, while its pressure is maintained constant, till the temperature corresponding to curve 4 is attained. The volume occupied by the gas will be diminished, its final state, represented by the point C, being reached by way of the horizontal straight line BC.

Now at B the substance exists as a gas, and at C it exists as a liquid, and yet no abrupt alteration occurs in the properties of the substance in passing from B to C. Hence Andrews concluded that the liquid and gaseous states are "*only distant stages of a long series of continuous physical changes.*"

If, after the condition represented by the point C has been attained, the pressure is gradually decreased, the temperature meanwhile being maintained constant, the substance will expand along the isothermal CD, and the point D will be reached. As the volume occupied by the gas is further increased, the appearance of a well-defined meniscus will denote that vaporisation is occurring. The pressure meanwhile remains constant, the condition of the substance being successively represented by the points on the line DE. At E the substance is wholly converted into vapour.

Cagniard de la Tour's Experiment.—As early as 1822, Cagniard de la Tour performed an experiment on the conversion of a liquid into a gas, which we can now explain. Let us suppose that a volume, represented by the abscissa of the point F (Fig. 97), is occupied partly by a liquid and partly by its saturated vapour. If the temperature is raised, the volume remaining constant, the substance will pass through the conditions represented by the line FG. If the liquid originally occupied so small a fraction of the total volume, that its thermal expansion does not cause it to entirely fill the space before the critical temperature corresponding to curve 6 is attained, the substance will at that temperature pass from the liquid to the gaseous state. To realise these conditions experimentally, it is only necessary to fill a strong tube with liquid, boil about a third of this off, and then seal up. The tube can then be placed in a bath and heated.

The apparatus used by Cagniard de la Tour is represented in Fig. 98. This consisted of a long tube, one end of which, A, was filled with air to indicate the pressure, whilst the other end was bent round and fused on to a wide closed tube, B, containing the liquid and its saturated vapour. The air was separated from the liquid and its vapour by means of mercury, which filled the rest of the apparatus. When the whole was heated, the changes which took place were slightly more complicated than those previously explained by the aid of Fig. 97, since both the volume and

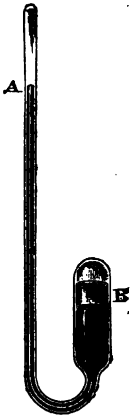

FIG. 98.—Cagniard de la Tour's apparatus for determining the critical temperature of a liquid. (P.)

the pressure of the liquid and its saturated vapour were varied. However, it was observed that as the temperature was raised, the surface of the liquid gradually became flatter, indicating that the surface tension was diminishing. When a certain temperature was reached, the surface suddenly disappeared, so that the space above the mercury in B appeared to be filled with a homogeneous gas. This temperature was the critical temperature of the substance. The disappearance of the surface corresponded to the passage through G from the cross-hatched to the unshaded portion of Fig. 97.

EXPT. 53.—*To determine the critical temperature of sulphur-dioxide.*—Take a piece of thick-walled thermometer tubing of about 2 mm. bore;

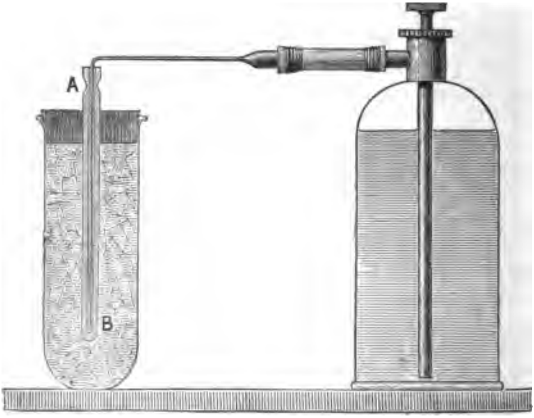

FIG. 99.—Arrangement for filling a tube with a mixture of liquid and vapour of sulphur-dioxide.

seal this at one end, and draw it out somewhat at a point A, Fig. 99, about 8 inches from the sealed end. Do not constrict the internal bore more than you can help in this process.

Take a piece of thin-walled glass tubing, and draw this out into a capillary tube, fine enough to pass down to the bottom of AB. Bend the capillary tube at right angles, and connect the wide tube in which it ends with the delivery tube of a bottle containing liquid sulphur-dioxide. Such bottles can be obtained from dealers in chemicals.

Take a wide test tube (or boiling tube), and having provided this with a cork bored to receive AB, Fig. 99, nearly fill it with a mixture of three parts (by weight) of broken ice to four parts of calcium chloride. Push AB (Fig. 99) through the hole provided in the cork, and arrange that the constricted part of the thermometer tube projects a little way above the latter. Place the capillary tube in position, and the arrangement will resemble that shown in section in Fig. 99.

On opening the valve of the bottle, liquid sulphur-dioxide will pass through the capillary tube and collect in the experimental tube. When this latter is nearly full close the valve and remove the capillary tube, and seal the experimental tube off at A by means of a small but very hot blowpipe flame. Some of the sulphur-dioxide will boil off during this process, but the tube should retain about two-thirds of its initial contents when the sealing has been effected.

Support the tube so that it is entirely immersed in a beaker about two-thirds full of glycerine, a thermometer reading to 200° C. being provided to indicate the temperature of the latter. Heat the glycerine by means of a Bunsen burner, and notice at what temperature the meniscus in the experimental tube disappears. Then allow the glycerine to cool, and note the temperature at which the meniscus once more becomes visible. The mean of these two temperatures may be taken as the critical temperature of sulphur-dioxide.

The pressure corresponding to the point G (Fig. 97) is termed the critical pressure of the substance.

Thus, it is impossible to liquefy a gas at a temperature higher than its critical temperature, and in order to liquefy it at that temperature a certain pressure, called the critical pressure, must be applied.

Pressure of Saturated Vapours.—It will be seen from Fig. 97, as well as from Andrews's curves, that when a vessel at a certain temperature is filled partly with liquid and partly with the vapour of that liquid, a certain definite pressure will be exerted by the vapour. This pressure corresponds to the ordinate of the horizontal straight line forming part of each isothermal for temperatures below the critical temperature. It is the greatest pressure which the vapour can exert at the given temperature, and is therefore termed the maximum vapour pressure (sometimes simply the vapour pressure) of the substance at the given temperature. The term "vapour tension" is also sometimes applied to the same value.

When the vapour pressure of a substance becomes equal to the pressure of the atmosphere, bubbles of vapour are formed in the interior of the liquid, and ebullition occurs.

Liquefaction of Gases.—Such gases as ammonia, sulphur-dioxide, &c., which should properly be classed with vapours, their critical temperatures being higher than the ordinary temperature of the atmosphere, may be liquefied either by merely subjecting them to high pressures, or by cooling them to low temperatures at atmospheric pressure. In other cases it is necessary not only to reduce the temperature below the critical value for the gas, but to apply a certain pressure. All known gases have now been liquefied, in most cases in large quantities. Some of the methods used, as far as these are related to the principles explained in this chapter, will be now described.

Faraday's Method.—We may take the liquefaction of chlorine as typical of the methods employed by Faraday. The substances from which chlorine gas could be evolved were placed at one end of a strong bent glass tube, closed at both ends; the other end of this tube was immersed in a freezing mixture. The temperature of the freezing mixture being below the critical temperature of the gas, the pressure produced by the rapid evolution of the gas was sufficient to effect liquefaction.

This method was successfully employed by Faraday, in 1823, in the liquefaction of nitrous oxide, hydrochloric acid, cyanogen, chlorine, &c.

Liquefaction of Carbon-Dioxide.—In 1834 Thirlorier liquefied carbon-dioxide in the following manner. A strong copper cylinder, lined with lead, and strengthened with external iron bands, was filled to about a third of its height with bicarbonate of soda. Sulphuric acid was contained in an open tube placed in the cylinder (Fig. 100). The top being screwed on, the cylinder was inverted, when the acid became mixed with the bicarbonate of soda, producing a copious evolution of carbon-dioxide. The pressure produced is sufficient to liquefy the gas at ordinary temperatures. Referring to Andrews' curves, Fig. 96, it may be seen that a pressure of 50 atmospheres is sufficient for this purpose at a temperature of about 13° C.

The inside of the generating cylinder was then put in connection with the interior of another vessel, kept at a lower temperature. The carbon-dioxide distilled over into the latter, just as the water distils from one bulb to the other in Wollaston's cryophorus (p. 184).

When carbon dioxide is allowed to escape, under great pressure, through a narrow orifice into a metal vessel open to the atmosphere, the cold produced is sufficient to produce carbonic acid snow. This slowly sublimes at a temperature of about −80° C. when exposed to the atmosphere. Mixed with ether, carbonic acid snow quickly evaporates, producing an exceedingly low temperature—about −77° C. This freezing mixture was used by Faraday in liquefying other gases.

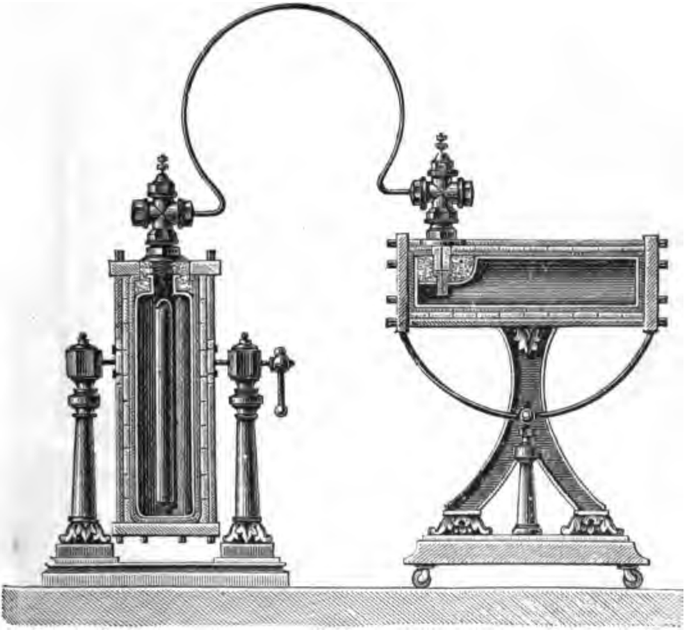

FIG. 100.—Arrangement used by Thirlorier to liquefy carbon-dioxide.

Cailletet's Method (1877).—A cylinder A, Fig. 101, strong enough to withstand a pressure of 1,000 atmospheres, was provided with an air-tight piston joined to the end of a square-threaded screw B. An internal screw thread was cut in the hub of a large wheel, C, the rim of which was provided with spokes to facilitate turning. When the wheel was turned the piston was forced into the cylinder. The latter was filled with water, and the pressure obtained by forcing the piston inwards was transmitted by water, which filled flexible copper tubes of small bore, to the manometer M and the experimental tube T.

A detail drawing of the experimental tube is given in Fig. 102. The gas to be compressed was contained in a glass tube of fine bore, the end of which dipped under the surface of some mercury. The pressure generated in the cylinder, Fig. 101, was transmitted to the water covering the surface of this mercury.

In order to liquefy a gas such as oxygen, the pressure was increased as far as possible and the gas was cooled by means of a jacket containing a suitable refrigerant, such as liquid sulphur-dioxide. The pressure was then suddenly released, and the expansion of the gas in the experimental tube caused its temperature to fall. A cloud of liquefied gas was formed, and lasted for a short time. Cailletet applied this method to the liquefaction of oxygen, carbonic-oxide and ethylene.

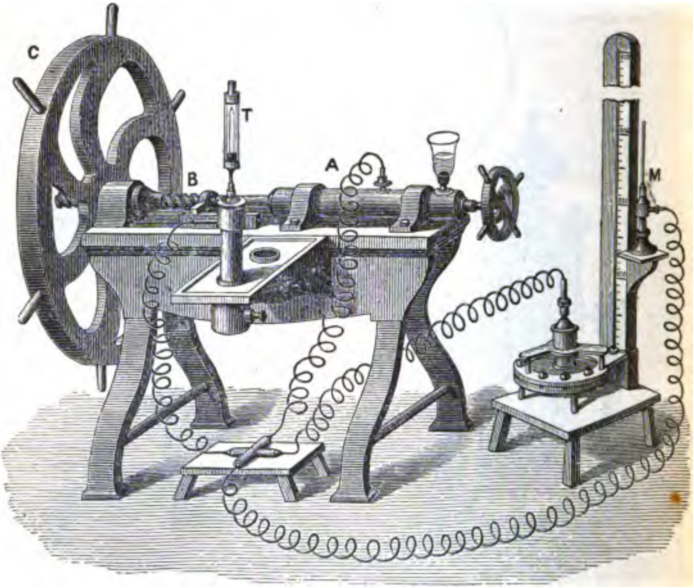

FIG. 101.—Cailletet's apparatus for liquefying oxygen.

Pictet's Method (1877).—The general principle of this method resembles those previously described. The arrangement used is represented diagrammatically in Fig. 103. Sulphur-dioxide gas was compressed by a pump A, and delivered in a liquid form into the cooling jacket CD. The vapour formed in the space above this liquid was pumped back into A. Thus rapid evaporation was produced, and a temperature of about − 70° C. was obtained in the jacket.

The pump B was used to compress carbon-dioxide gas, which was liquefied in the tube passing through the midst of the sulphur-dioxide jacket. The liquid carbon-dioxide was delivered into the cooling jacket EF, a temperature of − 130° C. being obtained by pumping the vapour there formed back into B.

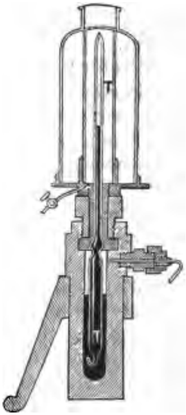

FIG. 102. — Cailletet's experimental tube.

A quantity of potassium chlorate was heated in a strong steel vessel V, the oxygen generated being forced into a tube passing centrally through the carbon-dioxide jacket. When a pressure of 500 atmospheres was indicated by the manometer M, liquefaction commenced. On opening the tap so as to permit the liquid to flow out, a white jet was observed, the liquid immediately evaporating. The first traces of liquid oxygen obtained by any method generally have a milky appearance, due to the presence of finely divided particles of solid carbon-dioxide. These may be removed by filtration through ordinary filter

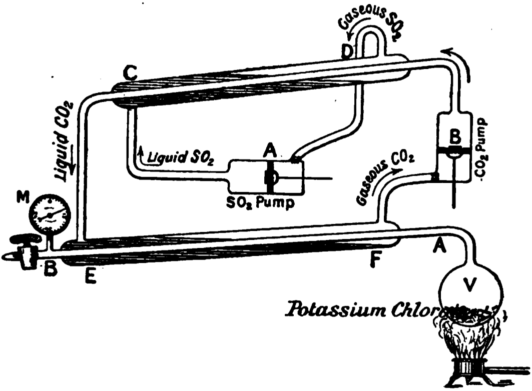

FIG. 103.—Pictet s method of liquefying oxygen.

paper, when the remaining liquid will be seen to be of a beautiful blue colour.

Wroblewski and Olszewski modified this arrangement by cooling liquid ethylene, first with a freezing mixture made from ice and salt, and then with a mixture of carbonic acid snow and ether. The liquid ethylene at a temperature of − 100° C. was led into a cylinder where its temperature was reduced to − 136° C. by rapid evaporation into a vacuum. A tube containing oxygen was immersed in the evaporating ethylene, and liquefaction was produced at a pressure of about 20 atmospheres.

A quantity of liquid air having been obtained, this was used as a cooling agent in an attempt to liquefy hydrogen. At a pressure of 100 atmospheres and a temperature of − 211° C., the hydrogen remained in the gaseous condition. On suddenly diminishing the pressure to which the hydrogen was subjected, a further cooling due to expansion was produced. The temperature in the hydrogen tube, after falling for a short interval, remained stationary, the pressure observed being 20 atmospheres; this was considered to indicate that the hydrogen had been liquefied. The temperature thus obtained, which was measured by the aid of a thermo-couple (see Chap. XIX.), was − 234° C.

Dewar's Experiments.—Using an improved form of the apparatus just described, Professor Dewar has been able to obtain large quantities of liquefied oxygen and air. Liquid oxygen was found to be of a beautiful blue colour, and to boil under atmospheric pressure at − 182° C. Nevertheless it can be poured into the palm of one's hand, if that is perfectly dry, and allowed to evaporate without any sensation of intense cold. The liquid, in fact, assumes the spheroidal condition (Chap. VIII., p. 195).

It was further found by Professor Dewar that if the liquid oxygen be poured into a glass vessel provided with double walls (Fig. 104), the space between the walls having been previously thoroughly exhausted, the liquid can be maintained in a stable state and its properties examined. The trace of mercury vapour contained in the vacuous space is condensed into a mirror on the walls of the vessel, and this further diminishes the rate at which radiation occurs (Chap. XXI.).

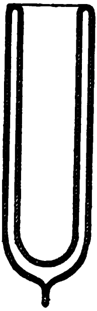
FIG. 104.—Section of Dewar's vacuum vessel.

Quite recently (1897), by the use of an improved form of Dr. Linde's apparatus, which will be described subsequently (Chap. XVIII.), Professor Dewar has been able to liquefy considerable quantities of hydrogen. Pictet thought that he had liquefied, and even solidified hydrogen, but it is now evident that he could not have done so, since he obtained a blue liquid, whilst that obtained by Dewar is transparent. Olszewski relied only on the evidence of a constant temperature to denote that he had liquefied hydrogen. The credit therefore rests with Professor Dewar for actually obtaining and examining the properties of liquid hydrogen.

A piece of metal immersed for some time in liquid hydrogen, and then suspended in the atmosphere, was found to quickly become coated with a white layer of solid air; after a few moments liquid air commenced to drip from it.

Helium, which Olszewski failed to liquefy, has also been liquefied by Professor Dewar.

Solid Hydrogen.—Later still (see *Nature*, Sept. 21, 1899) Professor Dewar has succeeded in solidifying hydrogen. A small double-walled test-tube, similar to that shown in Fig. 104, was filled with liquid hydrogen, and suspended in liquid hydrogen contained in a larger double-walled tube. The pressure was then reduced to 10 mm. of mercury, when rapid evaporation, accompanied by a fall of temperature, resulted (see p. 184). No solidification occurred, although it was afterwards found that the temperature reached was below the freezing point of hydrogen. This was an instance of *overcooling* (see p. 166–7). When a small trace of air was allowed to leak into the apparatus, the liquid hydrogen solidified into a solid foam. In further experiments a small amount of hydrogen, in the form of a transparent solid, was obtained. Its melting point was 16° absolute, (−257° C.). The critical temperature (see p. 207) of hydrogen is between 30° and 32° absolute (between −241° and −243° C.). The maximum density of liquid hydrogen was found to be 0·086 grams. per c.cm.

Uses of Liquefied Air.—When air is liquefied, both the oxygen and the nitrogen pass into the liquid state simultaneously. If, however, liquid air is allowed to slowly evaporate, nitrogen passes off in greater quantities than oxygen. Thus the liquid which remains becomes richer in oxygen as evaporation proceeds. Hence an economical method of liquefying air would furnish us with a ready means of procuring comparatively pure oxygen (*see* Chap. XVIII.).

By allowing a quantity of liquid air to slowly evaporate, and examining the spectrum of the last traces of gas given off, Professor Ramsay and Dr. Travers have discovered two new constituents of atmospheric air, which they have named *krypton* and *xenon*.

The first traces of gas given off during the slow evaporation of liquefied argon, were further found to contain a new gas to which the name *neon* has been given.

The scientific value of liquid air chiefly lies in its efficacy as a cooling agent. Professor Dewar has been able to prove that at – 180° C., chemical reactions can no longer take place. Bacteria, as well as many seeds, retain their vitality after a protracted cooling in liquid hydrogen.

Professors Dewar and Fleming have also investigated the electrical resistance of various pure metals and alloys at low temperatures. The interesting discovery has thus been made that the resistance of a pure metal decreases as the absolute zero of temperature is approached. Thus at – 223° C., copper and iron become almost perfect conductors, very little alteration being produced during further cooling. Platinum practically reaches its maximum conductivity at – 240° C.

Another unexpected result obtained by Professor Dewar is that if cotton wool, eggshells, leather, &c., are dipped in liquid air, and then exposed for a few moments to light, they will be found to phosphoresce brightly on being placed in a dark room.

Substances like lead, which are not elastic at ordinary temperatures, have been found by Professor Dewar to become elastic on cooling in liquid air. India-rubber and iron, when similarly cooled, become as brittle as glass.

(For some remarks on certain unjustifiable claims which have recently been made in connection with methods of producing and utilising liquid air, see Chap. XVIII.)

SUMMARY.

Careful experiments have shown that in no substance is Boyle's Law accurately obeyed. In the case of hydrogen, pv increases with the pressure. In the case of nitrogen, pv at first decreases and subsequently increases with the pressure. Other gases show a similar variation of pv with the pressure.

Isothermals of Carbon-dioxide.—Andrews proved that for temperatures below 30·92°C. the isothermals of carbon-dioxide possessed a discontinuity corresponding to the formation of liquid. The pressure of the vapour was constant during liquefaction at a given temperature. Above 30·92°C. no discontinuity of the isothermals could be traced, and liquefaction could not be induced.

Critical Temperature.—Above a certain definite temperature a gas cannot be liquefied, however much the pressure may be increased. This temperature is termed the critical temperature. Above the critical temperature a substance exists as a gas. Below the critical temperature, the substance may exist either as a liquid or as a vapour.

Continuity of State.—Andrews concluded that the liquid and gaseous states are "only distant stages of a long series of continuous physical changes."

Liquefaction of Gases.—Substances such as ammonia, sulphur-dioxide, &c., of which the critical temperature is higher than the ordinary atmospheric temperature, may be liquefied by pressure alone. The so-called permanent gases must first be cooled below their critical temperatures, and then liquefied by the application of a sufficient pressure.

Liquid Air or Oxygen can be preserved for considerable intervals of time if placed in vessels provided with double walls, the space between the walls being exhausted.

QUESTIONS ON CHAPTER IX.

(1) Define the critical temperature, pressure, and volume of a vapour, and give some account of the behaviour of a substance near its critical point.

(2) Give some account of investigations on the relation between the temperature and the divergence of the actual compressibility of a gas from that which would be reduced from Boyle's Law; discuss also the conclusions which these investigations support.

(3) Define the critical point of a fluid. Give sketches of, and point out the difference between the forms of, the isothermals of carbonic acid above and below its critical point.

(4) Describe the apparatus used in the liquefaction of oxygen.

(5) Describe researches which have been made to find the value of pv for various gases through a wide range of pressure at constant temperature, and give some account of the results.

(6) Describe Andrews' experiments on carbon dioxide, and explain the terms: critical pressure, critical temperature, and critical volume. Can a body be at the critical pressure and not at the critical temperature?

(7) Sketch the isothermal lines for carbonic acid from 20° to 50°C., and state what is meant by terms: critical temperature, critical pressure, and critical volume.

CHAPTER X

PROPERTIES OF VAPOURS

Saturated and Unsaturated Vapours.—The physical meaning of the distinction drawn in the last chapter between saturated and unsaturated vapours may be made clearer by the following considerations. Let us suppose that we are provided with a vessel, the volume of which can be varied at will, and that into this vessel, initially entirely exhausted, a drop of liquid, say water, is introduced. If the volume of the drop of water is very small in comparison with the volume of the vessel, the water will almost immediately evaporate, and the vessel will be filled with aqueous vapour. This vapour will exert a certain pressure on the walls of the vessel, and if the volume of the vessel be varied, it will be found that the product of the pressure and volume of the vapour remains approximately constant. The vapour in the vessel is now in an *unsaturated* condition.

If a comparatively large quantity of water is introduced into the vessel, only a part will evaporate. Any diminution in the volume of the containing vessel will now produce no alteration of pressure. A part of the vapour will be condensed, and the remainder will be in exactly the same condition as before. The vapour is now in a *saturated* condition. The pressure which it exerts depends only on its temperature, and not, as in the case of an unsaturated vapour, on both the temperature and volume.

EXPT. 54.—*To determine the relation between the pressure and volume of an unsaturated vapour.*

The apparatus constructed for the purpose of determining the relation between the pressure and volume of a gas (see p. 90) may be used for this experiment. The burette must, however, be shifted from the position occupied in Fig. 45, and placed as high as possible, the drying tube being removed.

Remove the plug of the stop-cock, and after having cleaned this with benzene, close, by means of plaster of Paris, one end of the hole bored through it. Thus, a small hole closed at the bottom will be left on one side of the plug. Cover the exposed surfaces of the plaster with a thin layer of shellac varnish, and heat gently to dry the latter.

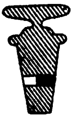

FIG. 105.—Section of plug of stop-cock, arranged for Expt. 54.

If, now, after the plug has been replaced, a small funnel filled with water is attached to the nozzle of the stop-cock, each time the plug is turned completely round, a small quantity of water will be discharged into the burette, without the interior of the latter being thereby put into communication with the atmosphere.

Before the plug is replaced, raise the mercury reservoir till the mercury in the burette begins to overflow. Replace the plug, after filling the hole in it with water, and attach a funnel as above described. Now lower the reservoir. If the hole in the funnel is not in communication with the burette, and the mercury is dry, no motion of the mercury in the burette will take place till the surface of the mercury in the reservoir is depressed below the stop-cock by a distance equal to the pressure of the atmosphere, measured in centimetres of mercury.

Adjust the reservoir so that the surface of the contained mercury is about 76 cms. below the stop-cock. Now turn the plug of the latter so that a small quantity of water is discharged into the burette. The surface of the mercury in the burette immediately sinks, owing to the formation of vapour. Determine the relation between the volume and pressure of the latter, proceeding as when proving the truth of Boyle's Law (p. 93). The only difference in the method used is, that in the present case the difference in level between the mercury surfaces in the burette and reservoir must be subtracted from the atmospheric pressure, as read by the aid of a barometer, instead of being added, as previously.

EXPT. 55.—*To show that the pressure of a saturated vapour in presence of the liquid from which it originated is independent of the volume which the two occupy.*

If the plug of the stop-cock, arranged as in the previous experiment, be turned round several times, water may be discharged into the burette till some of it remains unevaporated. When this has been done, show that the surface of the mercury in the burette is always at a certain constant height above the surface of the mercury in the reservoir, whatever volume is occupied by the liquid and its saturated vapour.

The Pressure exerted by the Saturated Vapour of a Substance is termed the Vapour Pressure (sometimes the Vapour Tension) of that Substance.

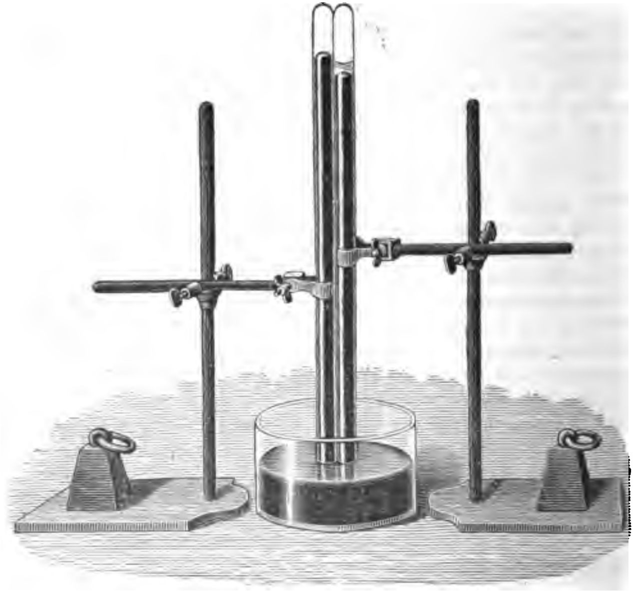

FIG. 106.—Arrangement for determining the vapour pressure of a liquid.

EXPT. 56.—*To determine the vapour pressure of a given liquid.* This might be done after the manner described in the last experiment. The following is, however, the more usual method of procedure.

Take two pieces of glass tubing, each of about 1 metre in length and a little less than 1 cm. in diameter. Clean the internal surface of these with strong nitric acid, then rinse with distilled water, and pull plugs of cotton wool through them, and finally dry by sucking air through them whilst they are heated. Seal one end of each of these tubes.

Take some clean mercury and warm this in an evaporating basin until a small drop of distilled water placed on its surface immediately boils off. When thoroughly cooled, pour some of this mercury into one of the tubes until this is filled to within about half a centimetre of the open end. Close this end with the thumb, and tilt the tube so that the enclosed air may pass slowly down its sides, thus collecting the small bubbles of air which will be found there.

When all the air bubbles have been removed, completely fill the tube with mercury, close its open end with the thumb, and, after inverting it, place the orifice below the surface of some mercury contained in a suitable vessel, when the thumb may be removed.

Repeat this operation with the other tube, inverting it over the vessel of mercury already used. Support both tubes vertically side by side with the aid of retort stands (Fig. 106), taking care that there is a small space between the extremities of the tubes and the bottom of the vessel containing the mercury.

Make a bent pipette (Fig. 107), fill this with the liquid of which the vapour pressure is required, and place the opening of the curved end under the extremity of one of the tubes. Blow cautiously into the pipette, so as to force a few drops of the liquid into the mercury contained by the experimental tube. The liquid will rise through the mercury, and immediately it reaches the surface the latter will be depressed. When a layer of liquid about a millimetre deep lies over the surface of the mercury, the difference in the level of the mercury in the two tubes can be measured; the value thus obtained is the vapour pressure of the liquid at the temperature of the air of the room.

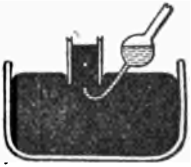

FIG. 107.—Method of introducing liquid into experimental tube.

Vapour Pressure in an unequally heated Vessel.—Referring to the drawing of Wollaston's Cryophorus (Fig. 82, p. 184), it will be remembered that the vapour condenses in the cold bulb A, whilst the liquid in the warmer bulb evaporates. Thus, vapour will pass into A, accompanied by a progressive cooling of the remaining liquid, till a uniform temperature is attained. During the intermediate stages, the mean pressure in the enclosure will differ only slightly from that in the colder bulb, the difference in pressure in the two bulbs being only sufficient to keep up the flow of vapour from one to the other. Hence it becomes most important in determinations of vapour pressure to keep the temperature of the whole of the space occupied by the liquid and its vapour as uniform as possible. The vapour pressure obtained will otherwise correspond to the lowest temperature at which any part of the enclosure stands.

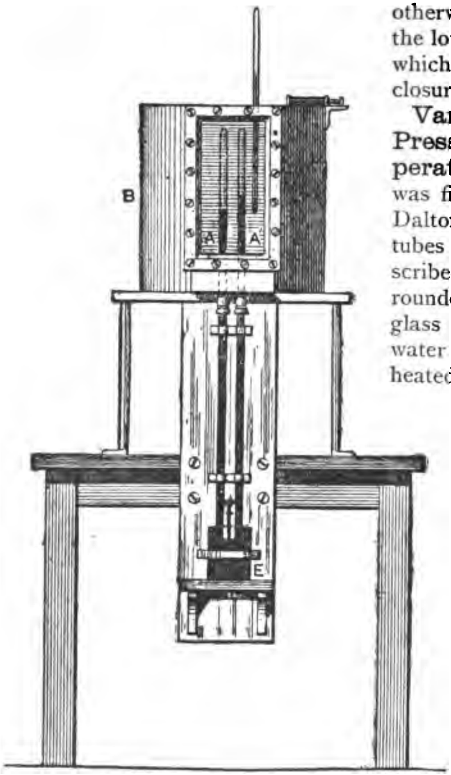

FIG. 108.—Regnault's vapour-pressure apparatus.

Variation of Vapour Pressure with Temperature.—This subject was first investigated by Dalton, who used two tubes similar to those described above, but surrounded by a cylindrical glass vessel filled with water which could be heated to any required temperature. Thermometers were placed at various heights in the water, and the vapour pressure measured was assumed to correspond to the mean of the temperatures thus indicated.

Inaccuracies were thus introduced, owing:

1. To the lowest temperature of any part of the vapour not being known;
2. To errors in reading introduced by irregularities in the glass of the cylindrical water jacket.

Regnault's Experiments.—In order to avoid errors due to the above causes, Regnault surrounded only the upper portion of the two tubes with a water bath. This latter took the form of a very large vessel, B, Fig. 108, provided with an efficient stirring arrangement. A window of plate glass was provided in front, so that observations could be made with accuracy. Errors due to refraction in the liquid or the glass did not amount to ·1 mm. The difference in height of the mercury in the two tubes was observed by means of a cathetometer.

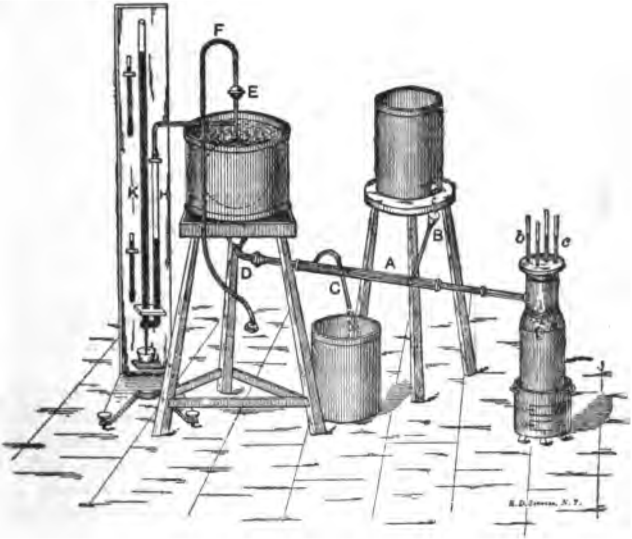

FIG. 109.—Regnault s vapour-pressure apparatus, for high temperatures.

Experiments at very high Temperatures.—Regnault found the arrangement just described to be unsuitable for temperatures at which the vapour pressure of the substance to be examined was more than 300 mm. Accordingly he used the arrangement represented in Fig. 109, when high temperatures were in question. A strong copper boiler was partly filled with the liquid to be experimented on, the temperature of the liquid and that of its vapour being observed by the aid of four thermometers, *b*, *c*. The upper part of the boiler was connected, by means of a tube, with a large hollow metal sphere immersed in a water bath kept at a constant temperature. This sphere was filled with air, the pressure of which could be varied by the aid of a pump, and measured by means of an open mercury manometer KH. The vapour given off from the boiling liquid was condensed by a cold water jacket AC, and the liquid thus formed flowed back into the boiler.

The principle involved in this experiment is somewhat different from those previously described. When the liquid is boiling, the pressure of its vapour must become equal to that of the air in the sphere. For, if the pressure of the vapour were greater than that of the air in the sphere, vapour would be forced into the latter till the two pressures were equalised. Similarly it can be shown that the pressure of the vapour in the boiler could not permanently be less than that of the air in the sphere. In fact, the air in the sphere merely served to transmit the pressure of the vapour to the manometer KH, having the advantage that it was not condensed when cooled to a low temperature.

Great accuracy was attained by the use of this apparatus. The pressure having been adjusted, and the stove lighted, boiling commenced, and after a short time the thermometers indicated a stationary temperature. Pressures varying from a small fraction of an atmosphere up to 28 atmospheres were thus measured.

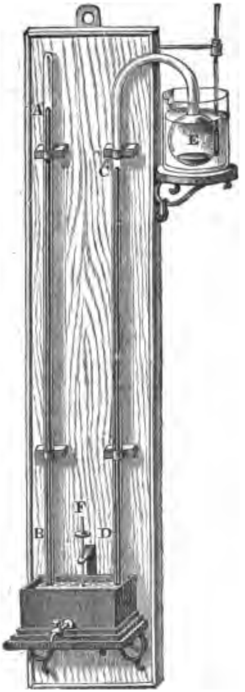

FIG. 110.—Gay-Lussac's vapour-pressure apparatus, for low temperature. (P.)

Vapour Pressure at Low Temperatures.—Gay-Lussac conducted a series of experiments to determine the vapour pressures of substances at temperatures below 0° C., using a modified form of the arrangement originally employed by Dalton. The vapour tube CE was bent round near its upper extremity, and ended in a bulb E (Fig. 110). The liquid to be experimented on was contained in this bulb and was reduced to low temperatures by immersing the bulb in a freezing mixture. A liquid freezing mixture was preferred, since stirring could be effected and a constant temperature be thus maintained.

It has already been pointed out (p. 224) that the vapour pressure observed under the conditions at present under consideration will correspond to the temperature of the coldest part of the enclosure: in the present instance to that of the bulb and freezing mixture.

Comparison of Vapour Pressures.—A simple but extremely elegant piece of apparatus designed for the purpose of comparing the vapour pressures of two liquids at various temperatures, has recently been described by Dr. Lehfeldt. It consists of a glass tube A (Fig. 111), bent round so that two portions of it lie parallel to each other and very close together, their continuations being bent twice at right angles, and ending in bulbs C, C′. Pieces of thermometer tubing are sealed on to the bulbs C, C′, and another piece is sealed on to the main tube at B.

The method of filling this apparatus is as follows. The inside of the tubes having been cleaned and dried, the capillaries D, D′ are drawn out and sealed. The tube connected at B is drawn out at B′; and the piece of thermometer tubing left below the constriction B′ is connected with a mercury vacuum pump. The whole apparatus is then thoroughly exhausted, the tubes being heated to remove the gases condensed on their walls. The apparatus is then sealed at B′, a short length of capillary tube being left above this point.

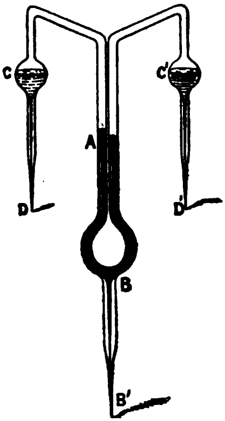

FIG. 111.—Dr. Lehfeldt's apparatus for comparing the vapour pressures of two liquids.

If, now, the size of the capillary B′ is properly chosen, on breaking off its end below mercury the latter will slowly flow into the gauge A, and when sufficient has entered, the capillary can be sealed off by the aid of a blow-pipe. In a similar manner the bulbs C,C′ can be partially filled with the liquids of which the vapour pressures are to be compared.

The whole arrangement can then be placed in a bath and heated to any desired temperature; the difference in level of the mercury surfaces in the gauge A gives the differences of the vapour pressures of the two liquids.

Vapour Pressure Thermometers.—The irregularities connected with the thermal expansion of the bulb of a mercury thermometer render the use of that instrument unsatisfactory where a high degree of accuracy is required. Even in the case of an air thermometer it is necessary for the most accurate work to apply corrections for the expansion of the containing vessel, or to employ some compensating arrangement, such as that due to Professor Callendar (Ch. V., p. 111). On the other hand, the pressure exerted by a saturated vapour is independent of the size of the containing vessel. Regnault has measured the

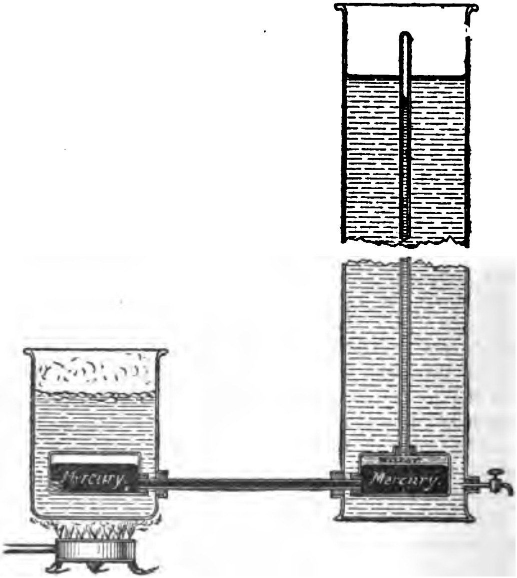

FIG. 112.—Lord Kelvin's Vapour Pressure Thermometer.

vapour pressures of a number of substances at various temperatures, and consequently a measurement of the vapour pressure of one of these substances suffices to determine its temperature, quite independently of any change of volume which may occur in the containing vessel.

Fig. 112 represents a vapour pressure thermometer for high temperatures (100° to 500° C.), designed by Lord Kelvin.[1] In this case the vapour pressure of mercury is measured by the aid of a long manometer tube containing water. The bulb of the thermometer is freed from air, and contains only mercury and its vapour. The pressure is transmitted from the bulb to the lower extremity of the manometer tube by means of a tube filled with mercury. In the arrangement represented, the space immediately above the water column is freed from air, so that the head of water gives the pressure of the mercury vapour. An open manometer tube might, however, be employed if the atmospheric pressure near the open end of the tube is determined for each observation. The water column is kept at a constant temperature by being surrounded by a vessel through which water at a constant temperature circulates.

The vapour pressure of mercury below 100° is too small to accurately indicate its temperature. Water vapour may be used between about 30° C. and 100° C., and for lower temperatures sulphur dioxide vapour may be employed.

Dalton's Law.—In 1801 Dalton formulated the law that the pressures of the saturated vapours of all liquids have the same value at temperatures equally removed from their boiling points. In the case of water, the vapour pressure at 80° C. (*i.e.*, 20° below the boiling point) is 355 mm. Ether boils at 35° C., and its vapour pressure at $(35 - 20)^\circ = 15^\circ$ C. is 354 mm. It was on this agreement that Dalton based his law. In the case of alcohol, however, which boils at 58° C., the vapour pressure at $(58 - 20)^\circ = 38^\circ$ C. is only 330 mm. Similar deviations occur with other liquids. Hence this law cannot be said to have been proved.

Pressure exerted by a Mixture of Gas and Vapour.—Regnault determined the pressure exerted by a vapour (1) when distributed through an otherwise empty space; and (2) when distributed through a space containing a quantity of a permanent gas. The apparatus used was similar to that represented in Fig. 108, p. 224. As a result, it was found that the pressure exerted by a vapour is practically the same whether the space through which it is distributed is otherwise empty or is occupied by a gas or gases. This law was found to apply to both saturated and unsaturated vapours.

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[1] *Encyclopædia Britannica*, art. "Heat."

The same law had previously been formulated by Dalton.

Example.—It is required to draw the isothermal for a mixture of saturated aqueous vapour and a perfect gas for a temperature of 50° *C.*

(Pressure of saturated aqueous vapour at 50° C. = 92 mm. of mercury.)

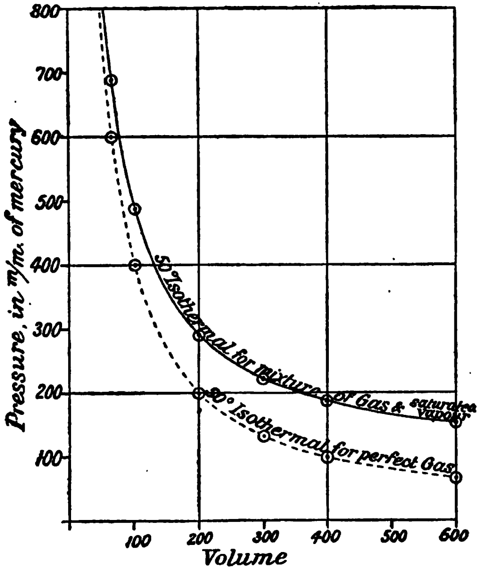

FIG. 113.—Isothermal for mixture of air and saturated vapour.

The dotted curve (Fig. 113) is the isothermal for a quantity of a perfect gas. This curve is represented by the equation

$$pv = K.$$

If a quantity of aqueous vapour, sufficient to saturate the largest volume occupied by the gas, is introduced into the space occupied by the latter, the pressure corresponding to any volume of the gas will be increased by the constant vapour pressure of water at the given temperature. Hence, if we measure distances equivalent to 92 mm. vertically above various points on the dotted curve, and join the points so obtained, the resulting curve will be the isothermal for the mixture of gas and vapour.

It will be noticed that the curve is less steep than the isothermal for the perfect gas. The reason of this is, that as the volume is decreased the aqueous vapour condenses, and the liquid occupies a negligibly small volume.

Example.—A quantity of hydrogen is collected over water in an inverted glass vessel, and the volume which it is observed to occupy is 356·5 c.cs. The barometer stands at 758 mm., and the surface of the water in the graduated vessel is 7 cms. above the level of the water in the trough. The temperature of the water is 17° C. What would be the volume of the hydrogen when dry at 0° C. and 760 mm. pressure?

The pressures of saturated aqueous vapour at various temperatures is given in a Table at the end of this book. From this we find that the vapour pressure for 17° C. is 14·4 mm. of mercury.

Since the water stands 7 cm. higher inside the graduated vessel than outside it, the pressure, in mm. of mercury, of the mixture of hydrogen and saturated aqueous vapour is equal to

$$758 - \frac{70}{13 \cdot 6} = 758 - 5 \cdot 1 = 752 \cdot 9 \text{ mm.},$$

where the density of mercury is taken equal to 13·6.

The pressure which would correspond to the same volume of dry hydrogen at 17° C. is equal to 752·9, *less* the pressure of the saturated aqueous vapour, *i.e.*, $752 \cdot 9 - 14 \cdot 4 = 738 \cdot 5$.

Hence we have the following problem to solve.

A quantity of dry hydrogen occupies a space of 356·5 c.cs. at a temperature of 17° C., and a pressure of 738·5 mm. of mercury. What volume will this gas occupy at 0° C., and a pressure of 760 mm. of mercury?

According to the relation established on p. 94,

$$pv = \text{RT}$$

where R is a constant, and T is the absolute temperature of the gas.

We therefore have, denoting by v the volume required,

$$\begin{aligned} 738 \cdot 5 \times 356 \cdot 5 &= \text{R} \times (273 + 17) = 290\,\text{R} \\ 760 \times v &= 273\,\text{R}. \end{aligned}$$

Eliminating R, by dividing the lower by the upper equation, we get

$$\frac{760 \times v}{738{\cdot}5 \times 356{\cdot}5} = \frac{273}{290}$$

$$\therefore \; v = \frac{273 \times 738{\cdot}5 \times 356{\cdot}5}{760 \times 290} = 326{\cdot}0 \text{ c.cs.}$$

Vapour Pressure of Liquid Mixtures.—Regnault found that the vapour pressure of a mixture of two or more volatile liquids is equal to the sum of the vapour pressures of the constituents, when these do not dissolve each other (*e.g.*, in the case of water and benzene). In the case of liquids which dissolve each other (*e.g.*, water and alcohol, water and ether), the vapour pressure of the mixture is less than the sum of the vapour pressures of the constituents, in some cases even less than the vapour pressure of one of the constituents.

Vapour Pressures of Solutions. Raoult's Law.—Experiments have shown that the vapour pressure of a solution of a non-volatile substance is always less than that of the pure solvent. It has already been pointed out that the boiling point of a solution of a non-volatile substance is higher than that of the pure solvent. Since the vapour pressure of a solution at its boiling point is equal to the atmospheric pressure, we see that the elevation of the boiling point produced by dissolving a non-volatile substance in a pure solvent is closely related to the diminution of the vapour pressure at a given temperature, produced under similar circumstances.

Raoult has shown that the diminution of the vapour pressure of a solution of a non-volatile substance is proportional to the number of molecules dissolved in 100 grams of the pure solvent, and is independent of the nature of the dissolved molecules. A reservation must be made with regard to aqueous solutions which conduct electricity, similar to that explained in connection with the molecular depression of the boiling point (*see* p. 191).

EXPT. 57. Make a strong aqueous solution of calcium chloride, and heat this to about 90° C. Place the bulb of a thermometer in the solution, and then blow steam through the latter. Observe the temperature indicated by the thermometer. It will be found that a temperature of about 112° C. is attained.

The result of this experiment is explained as follows:—The vapour pressure of an aqueous solution of calcium chloride at 100° is less than that of pure water at the same temperature. Consequently steam is condensed in the solution. But for each gram of steam condensed, 537 therms of heat are rendered up. The reception of this heat raises the temperature of the solution till its vapour pressure becomes equal to that of water boiling at 100°. In other words, the temperature of the solution rises until its boiling point is attained.

The Triple Point.—We may represent the relation between the temperature and pressure of saturated aqueous vapour by a curve, such as Fig. 114. For a particular temperature OB, and a corresponding pressure BA, a vessel may be occupied partly by water and partly by aqueous vapour, and no condensation or evaporation will occur. The water and its vapour are in equilibrium. If, however, whilst the temperature is maintained at OB, the pressure is raised to BC, a progressive condensation will occur till nothing but water remains.

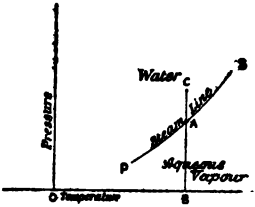

FIG. 114.—The steam line.

The conditions above assumed may be experimentally realised by enclosing water and its saturated vapour in a cylinder fitted with an air-tight frictionless piston. If the pressure tending to force the piston inwards is equal to the maximum vapour pressure of water of the temperature at which the cylinder is maintained, the piston will remain stationary, and the relative volumes of the water and its vapour will remain unaltered. If the external pressure on the piston is increased, the piston will move inwards till the whole of the vapour is condensed.

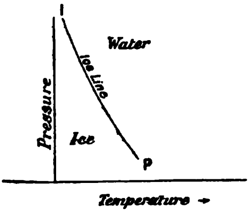

Fig. 115.—The ice line.

Hence, in a state of equilibrium, all points above the curve PS will correspond to the existence of nothing but water in the vessel, whilst similar reasoning may be employed to show that points below the curve PS will correspond to the existence of nothing but aqueous vapour in the vessel. The curve PS is called the **Steam Line.**

Lord Kelvin has shown, in verification of the hypothesis of his brother, Professor James Thomson, that the melting point of ice is lowered by increased pressure. Consequently for any particular pressure, ice will melt if it is above a certain temperature; or water will freeze if it is colder than that temperature. We may therefore draw a curve such as PI. Fig. 115, exhibiting the relation between the temperature and pressure at which a mixture of ice and water may remain in equilibrium, *i.e.*, without ice melting or water freezing. As a result of a train of reasoning similar to that employed above with regard to water and aqueous vapour, it may be shown that points above the curve PI will correspond, in a state of equilibrium, to the existence of nothing but water in the vessel, whilst points below PI correspond to the existence of nothing but ice in the vessel. PI is termed the **Ice Line.**

Another curve, PH, Fig. 116, may be drawn, exhibiting the relation between the pressure and temperature corresponding to a state of equilibrium between ice and aqueous vapour. For points immediately above HP, nothing but ice can exist in the vessel, whilst for points below HP, nothing but vapour can exist in it. HP is termed the **Hoar Frost Line.**

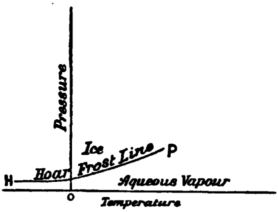

FIG. 116.—The hoar frost line.

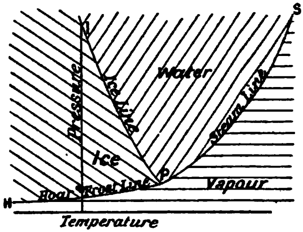

FIG. 117.—Triple point curves for water.

The above three curves represent relations between temperature and pressure, and therefore all three might be drawn in one diagram. This is done in Fig. 117.

Professor James Thomson proposed the theory that the steam line, the hoar frost line, and the ice line meet in a single point. Very simple reasoning will show that this must be the case.

For suppose that the curves intersected as shown in Fig. 118. Then, since the space ABC is above the steam line ACD, points in it must correspond, in a state of equilibrium, to the existence of nothing but water in the vessel. On the other hand, since the space ABC is below the hoar-frost line BAE, points in it must correspond to the existence of nothing but vapour in the vessel. Also, since ABC is below the ice line CBF, points in it correspond to the existence of nothing but ice in the vessel.

Hence the intersection of the steam line, the hoar-frost line, and the ice line in three different points leads to three different and mutually contradictory conclusions, based on the mere definitions of the curves. Therefore the three curves must meet in a single point P (Fig. 117).

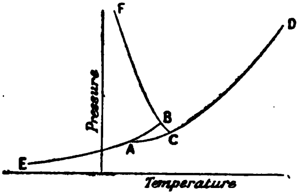

Fig. 118.—Impossible form of steam, hoar-frost and ice lines.

Regnault, as a result of his experiments on vapour pressure, concluded that the hoar-frost line was a mere continuation of the steam line. It was subsequently shown by Kirchhoff that the steam line and the hoar-frost line are distinct curves, meeting each other at an angle.

The conclusion reached, as a result of the above argument, is that at a certain temperature and pressure, defined by the point P, ice, water, and aqueous vapour can simultaneously exist in the same vessel without the occurrence of any alterations in their relative proportions. The point P is called the *triple point.* At this point the pressure of the saturated vapour of water is the same as that of the saturated vapour of ice.

At the temperature and pressure corresponding to the triple point, water may freeze and boil simultaneously. This condition may be realised by placing water in an exhausted vessel which also contains a dish full of strong sulphuric acid (*see* p. 184).

Example. Calculate the pressure and temperature corresponding to the triple point for water.

We will determine the co-ordinates of the point of intersection of the steam line with the ice line.

According to Dewar's Experiments (p. 179) an increase of one atmosphere lowers the melting point of ice by 0·0072° C.

Hence under zero pressure ice will melt at 0·0072° C.

It is easy to see that the temperature corresponding to the triple point will be between 0° C. and 0·0072° C. For ice cannot in any circumstances be formed above 0·0072° C.; and in order that ice should melt below 0° C., the pressure must be greater than one atmosphere.

Taking the standard atmosphere as equal to 760 mm. of mercury, we see that for a depression of 1° C. in the freezing point of water, the pressure must be increased by 105,000 mm. Therefore under a pressure of p mm. of mercury, ice will melt at $\left(0{\cdot}0072 - \frac{p}{105{,}000}\right)^\circ$ C.

At 0° C. the pressure of saturated aqueous vapour is equal to 4·60 mm., whilst at 1° C. the pressure amounts to 4·94 mm.

Therefore in the neighbourhood of 0° C., the pressure p corresponding to a temperature t° C. will be equal to $4{\cdot}60 + (4{\cdot}94 - 4{\cdot}60)t = 4{\cdot}60 + {\cdot}34t$.

$$p = 4{\cdot}60 + {\cdot}34t.$$

$$\therefore\ t = \frac{p - 4{\cdot}60}{{\cdot}34}.$$

The temperature t must be equal to the melting point of ice under a pressure of p mm. of mercury.

$$\therefore\ \frac{p - 4{\cdot}60}{{\cdot}34} = 0{\cdot}0072 - \frac{p}{105{,}000}.$$

$$\therefore\ 105{,}000p - 483{,}000 = 257{\cdot}108 - {\cdot}34p.$$

$$\therefore\ p(105{,}000 + {\cdot}34) = 483{,}000 + 257{\cdot}108.$$

$$\therefore\ p = \frac{483{,}257{\cdot}108}{105{,}000{\cdot}34}.$$

$$= 4{\cdot}60243 \text{ mm. of mercury.}$$

This is the pressure corresponding to the triple point. Substituting this value in the equation for the melting point of ice under a pressure p, we get, for the temperature t corresponding to the triple point

$$t = {\cdot}0072^\circ - \frac{4{\cdot}60243}{105{,}000} = {\cdot}0072 - {\cdot}000043 = 0{\cdot}007157^\circ \text{ C.}$$

Triple Point Curves for a substance which contracts on solidifying.

In Fig. 119 the boiling-point curve corresponds to the steam line in Fig. 117, whilst the sublimation curve corresponds to the hoar-frost line. The reasoning employed in connection with these curves is similar to that already used (pp. 233–5).

The melting-point curve corresponds to the conditions as to temperature and pressure under which a mixture of solid and liquid can be maintained in equilibrium with each other.

When a substance which contracts on solidifying is submitted to increased pressure, its melting point is elevated (p. 177). Consequently points above the melting-point curve will correspond to the solid state, and those below it to the liquid state. In other words, the melting-point curve will slope downwards from right to left (Fig. 119).

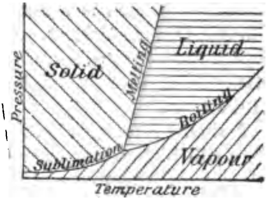

FIG. 119.—Triple point curves for a substance which contracts on solidifying.

It should be noticed that a substance which contracts on solidifying cannot exist in the liquid state at temperatures below that of the triple point. It can, however, be solidified at temperatures above that of the triple point.

On the other hand a substance (like water) which expands on solidifying cannot be solidified at temperatures above that of the triple point, but it can exist in either the liquid or solid state at temperatures lower than that of the triple point.

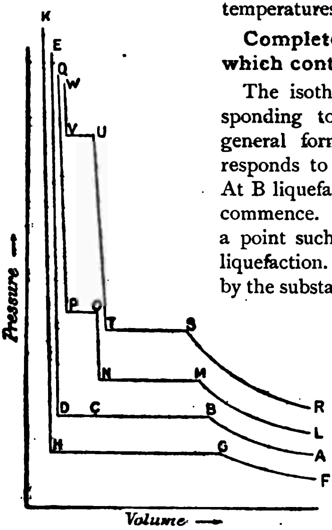

FIG. 120.—Isothermals of a substance which contracts on solidifying.

Complete Isothermals of a substance which contracts on solidifying.

The isothermal for the temperature corresponding to the triple point will be of the general form ABCDE (Fig. 120). AB corresponds to the state of unsaturated vapour. At B liquefaction or solidification, or both, may commence. If the substance is first liquefied, a point such as C will correspond to complete liquefaction. Diminishing the volume occupied by the substance produces solidification. Thus at D the substance is completely solidified. DE is the isothermal of the solid for the temperature corresponding to the triple point.

FGHK is an isothermal for a temperature *below* that of the triple point. GH corresponds to a mixture of solid and saturated vapour; no liquid can be formed at this temperature. HK corresponds to the solid state.

For temperatures *above* that of the triple point, the substance can only be solidified under high pressure. Thus LM corresponds to the state of unsaturated vapour.

MN corresponds to a mixture of liquid and saturated vapour. At N the substance is completely liquefied. When the pressure to which the liquid is subjected is increased to that corresponding to the point O, solidification commences. OP corresponds to a mixture of solid and liquid, the volume decreasing as solidification proceeds. At P the substance is completely solidified, and PQ corresponds to the isothermal of the solid.

A similar interpretation may be given of the isothermal RSTUVW, for a still higher temperature. Notice that at the temperature of the triple point the liquid and solid lines BC, CD, are at the same level. As the temperature is raised, the level of the line of solidification is farther and farther removed from the level of the line of liquefaction. Thus, the difference of level between VU and TS is greater than that between PO and NM.

There is probably a critical temperature above which a substance cannot be solidified. The pressure corresponding to this temperature would, however, be too great to permit of an experimental investigation of this point.

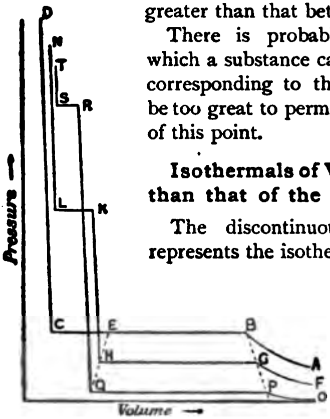

FIG. 121.—Isothermals of water for temperatures lower than the triple point.

Isothermals of Water for Temperatures lower than that of the Triple Point.

The discontinuous curve ABECD (Fig. 121), represents the isothermal of water for the temperature corresponding to the triple point. The curve from A to B corresponds to the state of unsaturated aqueous vapour. At B the vapour may commence to liquefy or to solidify, *i.e.*, to form water or hoar-frost, or both. From B to C ice, water, and saturated vapour may exist simultaneously. At E the whole of the vapour may have been converted into ice. Diminishing the volume liquefies this ice, and C corresponds to the existence of nothing but water. CD is the isothermal for water.

FGHKLN is an isothermal for a temperature lower than that corresponding to the triple point. At G the vapour commences to solidify, *i.e.*, to form hoar-frost. GH corresponds to a mixture of ice and vapour. At H nothing but ice remains. HK is the isothermal for ice. At K the ice commences to liquefy under pressure. KL corresponds to a mixture of ice and water. At L the whole of the ice is melted, and LN is the isothermal for water.

LN is to the right of CD. This signifies that water, when kept liquid by pressure at temperatures lower than 0°, increases in volume during cooling. (See p. 86.)

OPQRST is another isothermal for a still lower temperature. Its interpretation is effected after the manner explained in reference to the curve FGHKLN.

It is impossible to draw such a diagram to scale unless it is made very large. Fig. 121 is only intended to show the general form of the curves.

It will be noticed that the various isothermals cut each other. This simply means that under a given pressure, water can occupy the same volume at two different temperatures. The pressure and volume referred to are those corresponding to the intersection of the two curves.

Atmospheric Phenomena.—When the atmosphere is saturated with aqueous vapour, one or the other of the following phenomena may occur:—

1. **Dew.**—A cold object brought into contact with a mixture of air and saturated vapour causes a reduction in the temperature of the latter, resulting in the production of a state of over-saturation. Some of the vapour is condensed into water, which appears at first in minute drops on the cold object.

The amount of aqueous vapour in a particular part of the atmosphere, though perhaps insufficient to produce saturation at the temperature of the air, would suffice for saturation at a lower temperature. Thus, a cold object when brought into an unsaturated space, may cool the air near it to a sufficient degree for water to be deposited on its surface.

The water condensed on the surface of a cold object brought into contact with air containing aqueous vapour, is termed *dew*.

Dew Point.—That temperature at which the aqueous vapour distributed through a particular part of the atmosphere would suffice to produce saturation, is termed the dew point.

It is obvious that for dew to be deposited, the temperature of the cold object on which condensation takes place must be at or below the dew point.

2. **Mist.**—If a large quantity of air more or less saturated with aqueous vapour is gradually cooled, a temperature will ultimately be reached, at which the whole of the air is saturated. If small particles of matter are floating about in the air, the vapour will condense round these, forming small drops of water, which collectively constitute a mist.

Clouds.—If a mist is formed high up in the air, it is termed a cloud. The more or less saturated air rises from the surface of the earth, and becomes cooler by expansion on reaching high altitudes; or, by mixing with colder air, a state of saturation is attained, and a cloud formed.

EXPT. 58.—*To illustrate the formation of mist by causing saturated air to expand.*

Take a flask of about a litre capacity, clean its external and internal surfaces, and furnish it with a cork bored to admit a piece of glass tubing. Fasten a piece of india rubber-tubing to this glass tube, and introduce a layer of water about half a centimetre deep into the bottom of the flask. Allow this to stand for a time until the air has had an opportunity to become saturated.

On sucking air out of the flask, a momentary formation of mist will be noticed. This mist disappears if the exhaustion is maintained for a sufficient time, or if the pressure is allowed once more to attain its initial value.

Hygrometers.—An instrument designed to determine the amount of aqueous vapour in the atmosphere at any particular place and time, is termed a *hygrometer*.

The Hygrometric State of the Atmosphere is measured by the ratio :—

$$\frac{\text{Mass of aqueous vapour per c.c. of air at the observed temperature.}}{\text{Mass of aqueous vapour necessary to saturate one c.c. air at that temperature.}}$$

The usual methods of determining the hygrometric state of the atmosphere are more or less indirect, and depend on the determination of the dew point, or some similar physical magnitude. The principles underlying these methods are as follows :—

Let the temperature of the air be observed; then the mass of aqueous vapour which would saturate 1 cubic metre at that temperature can be obtained from the following table :—

Temperature in Centigrade Degrees.	Pressure of Saturated Vapour in mm. of Mercury.	Mass of Saturated Vapour per Cubic Metre.
0°	4·57	4·8
5	6·51	6·8
10	9·14	9·3
15	12·67	12·7
20	17·36	17·1
25	23·52	22·8
30	31·51	30·0
35	41·78	39·2
40	54·87	50·6

At the dew point, the aqueous vapour distributed through any space would just saturate that space. Hence, the mass of vapour actually present in a cubic metre of air can be obtained by determining the dew point; the required mass will be found in the third column of the above table, opposite to the temperature so obtained.

It will be noticed in the above table that the ratio of the masses of a cubic metre of saturated vapour at any two temperatures is very nearly equal to the ratio of the saturation vapour pressures for those temperatures. Hence the hygrometric state of the atmosphere is often expressed by the ratio :—

$$\frac{\text{Saturation Pressure of water vapour corresponding to the dew point temperature.}}{\text{Saturation Pressure of water for the temperature of the air during the experiment.}}$$

Dew Point Hygrometers.—In these instruments a surface is gradually cooled down till dew begins to be deposited, when the temperature of the surface is determined. In order to render the first appearance of dew plainly visible, it is best to use a polished silver surface.

Daniell's Hygrometer.—This consists of two bulbs, A and B, Fig. 122, connected by means of a tube bent so that the bulbs hang downwards. Some ether or other volatile fluid is placed in one of these bulbs, A, which is made of black glass; a thermometer which dips into it indicates the temperature. The rest of the enclosed space is exhausted of air.

In using this instrument, the ether is first run into the bulb A, and then a piece of muslin, wrapped round B, is moistened with ether. Rapid evaporation takes place, and the temperature of the bulb B is lowered. Consequently the vapour inside B is condensed, and evaporation takes place from the liquid in A, resulting in a fall in the temperature of the ether in A, and thence of the surface of the bulb.

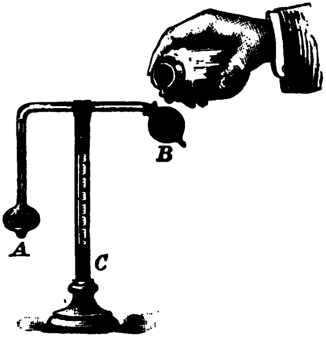

FIG. 122.—Daniell's Hygrometer.

When the surface of A has reached a temperature sufficiently low, a film of dew will be condensed on it; if cooling is discontinued, this film will soon disappear. The mean of the temperatures indicated by the enclosed thermometer when the dew respectively appears and disappears is taken as indicating the dew point of the surrounding atmosphere. The thermometer C indicates the temperature of the atmosphere.

Example.—With a Daniell's hygrometer, it was noted that a film of dew appeared when the enclosed thermometer indicated 9·5° C., and disappeared when it indicated 10·5° C. The temperature of the atmosphere was 15° C. What was the hygrometric state of the atmosphere?

Temperature of dew formation = 9·5°
,, ,, disappearance of dew = 10·5°

$$\therefore \text{Dew point} = \frac{9{\cdot}5 + 10{\cdot}5}{2} = 10^\circ$$

From the table on p. 241, we see that 1 cubic metre of saturated vapour at 10° C. has a mass of 9·3 grams.

Further, in order to saturate 1 cubic metre with aqueous vapour at 15° C., 12·7 grams of vapour are required.

Hence, hygrometric state of the atmosphere =

$$\frac{9{\cdot}3}{12{\cdot}7} = {\cdot}73.$$

Taking the ratio of the vapour pressures, we get as a value of the same quantity :—

$$\frac{9{\cdot}14}{12{\cdot}7} = {\cdot}72$$

Disadvantages of Daniell's Hygrometer.—Daniell's hygrometer suffers from the following disadvantages :—

1. It is difficult to regulate the rate of cooling of the bulb A.
2. Owing to glass being a bad conductor of heat, the temperature of the ether within the bulb A, which is indicated by the thermometer, will not be equal to the temperature of the external surface of the glass.
3. Some difficulty is experienced in noting the first appearance of dew on the black bulb.
4. The observer must stand near the instrument, and his breath will probably alter the hygrometric state of the atmosphere in that neighbourhood.

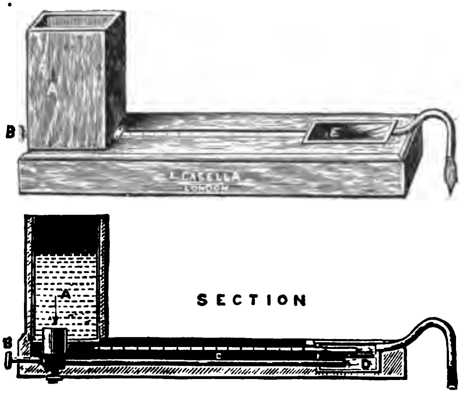

FIG. 123.—Dines's Hygrometer.

Dines's Hygrometer.—In this instrument, Fig. 123, water cooled with ice is contained in a vessel A, and is allowed to flow in a slow stream over a thermometer C. A thin plate of black glass (which might advantageously be replaced by a thin sheet of silver) is placed at E, immediately above the bulb of the thermometer. At the instant when a film of dew first appears on the plate, the temperature indicated by the thermometer is noted. The flow of the cold water is then interrupted, and the temperature indicated when the dew just disappears is observed. The mean of these two temperatures is taken as the dew point. The calculation to be performed in order to obtain the hygrometric state of the atmosphere is similar to that already explained.

Regnault's Hygrometer.—The essential parts of this instrument are shown in section in Fig. 124. A test tube A has its lower part removed and replaced by a vessel B made from thin sheet silver polished on its outside. A glass tube CD, passing through a sound cork which closes the mouth of the test tube, dips almost to the bottom of AB. The interior of AB is put into connection with an aspirator by means of a side tube EF.

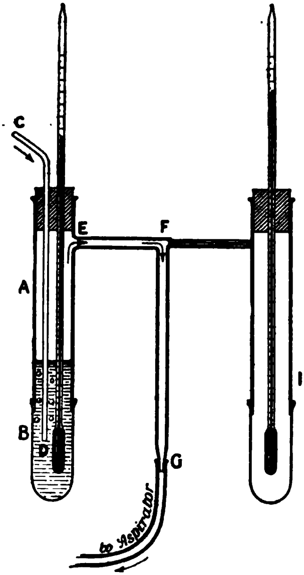

FIG. 124.—Regnault's Hygrometer (section).

Ether is poured into AB, and a current of air is drawn through this *via* CD, by the aid of an aspirator connected with the tube EFG. The evaporation of the ether, which can be controlled with the greatest nicety by adjusting the rate at which air is drawn through the apparatus, leads to a cooling of the ether; the temperature of the latter is indicated by a thermometer dipping into it. The polished external surface of B is watched from a distance by the aid of a telescope, and the instant that dew appears, the temperature indicated by the thermometer is read by the same means. A similar polished silver vessel is provided at the end of a tube K, for purposes of comparison. The thermometer enclosed serves to determine the temperature of the surrounding atmosphere.

The Wet and Dry Bulb Hygrometer.—When a piece of muslin, moistened with water, is exposed to the atmosphere, evaporation accompanied by cooling generally occurs. The *rate* at which the water evaporates will depend on the degree of saturation of the surrounding air; and as the rate of evaporation may be taken as representing the rate at which heat is leaving the liquid (being rendered latent in vaporising the water), the extent to which the water remaining on the muslin is cooled will depend on the hygrometric state of the atmosphere.

This principle is utilised in the wet and dry bulb hygrometer. The method of using this instrument will be made clear by the performance of the following experiment.

EXPT. 59.—*To construct a wet and dry bulb hygrometer, and determine by its aid the hygrometric state of the atmosphere in the laboratory.*

Take two thermometers and support these at a distance apart of three or four inches, in the manner shown in Fig. 125. Wrap a piece of muslin loosely round the bulb of one of these, and fold the lower part of this muslin round one end of a piece of lamp wick which has been boiled with washing soda to remove any grease. The other end of the wick dips into an evaporating basin containing a little water, placed some distance to one side of the thermometer.

To start the experiment, wet the muslin and the wick with water, and note the readings of both thermometers at short intervals of time. When stationary temperatures are reached, write these down.

Theoretical formulæ have been proposed to obtain the hygrometric state of the atmosphere from the respective temperatures indicated by the wet and dry bulb thermometers. These are of little importance, since the phenomena which occur during the experiment are too complicated to lead to a simple and yet satisfactory expression.

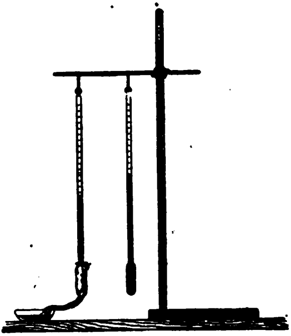

FIG. 125.—Wet and dry bulb hygrometer.

Tables have, however, been constructed, showing the relation between the temperatures indicated and the vapour pressure as determined by the aid of hygrometers such as have already been described. Such a table is given at the end of the book.

Example.—On a certain day the wet and dry bulb thermometers indicated 13° C. and 15° C. respectively. Determine from this the hygrometric state of the atmosphere.

Dry bulb reading = 15° C.

Difference in reading between wet and dry bulb thermometers = 2°.

From the table, in the horizontal row corresponding to a dry bulb reading of 15°, and in the column under 2°, we find that the pressure of the vapour in the atmosphere amounted to 10·1 mm.

∴ From the table on p. 241 we find that the pressure of saturated aqueous vapour at 15° = 12·7 mm.

∴ Hygrometric state of the atmosphere $= \frac{10\cdot 1}{12\cdot 7} = \cdot 80.$

Direct determination of the Mass of Aqueous Vapour in a given Volume of Air.

EXPT. 60.—Take a large bottle, such as is shown in Fig. 126, and nearly fill it with water.

If the stop-cock be opened, air will be drawn into the bottle as the water leaves it; and if the water be collected in a graduated measuring vessel, the volume of the air drawn into the bottle becomes known.

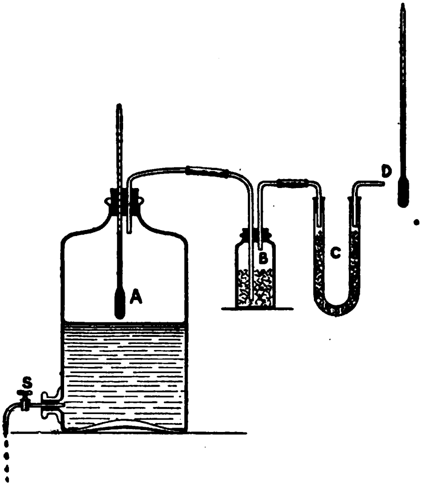

FIG. 126.—The chemical hygrometer.

Obtain a U-tube and fill each limb to within about an inch of the top with a mixture of phosphorus pentoxide and broken glass in large pieces. Close its extremities with india-rubber stoppers provided with bent glass tubes (Fig. 126). These latter should be pushed into pieces of india-rubber connecting tube, which are closed at the other ends by pieces of glass rod.

Obtain a bottle with a wide mouth and close this with a cork bored to admit two glass tubes. One of these tubes dips to the bottom of the bottle, whilst the other descends only a short distance below the cork. Fill this bottle about half way up with a mixture of large pieces of broken glass and phosphorus pentoxide. Insert the cork and close the ends of the glass tubes by the aid of india-rubber tubes provided with pieces of glass rod.

Weigh the U-tube on a chemical balance. Then connect up as indicated in Fig. 126. The pieces of glass rod, which serve to exclude the atmosphere from the phosphorus pentoxide, should not be removed until absolutely necessary. Finally, the end D of the tube communicating with the U-tube is opened, and the stop-cock S is turned so as to allow a gentle stream of water to issue forth. The phosphorus pentoxide in the bottle B prevents moisture from reaching the interior of the U-tube from the damp air in A. Hence the moisture which is absorbed in C will be wholly derived from the air which has passed into A.

When a sufficient volume of water has been drawn off, close the stop-cock and remove the U-tube, closing its ends with the same pieces of india-rubber tube and glass rod as were previously used. The amount of moisture condensed in the U-tube can be ascertained by weighing. Read the thermometers which indicate the temperature of the external air, and that in A.

Now, as a first approximation, we may say that the mass m of aqueous vapour which has been condensed in the U-tubes was distributed in the external atmosphere, through a volume V, equal to the volume of the water which has been drawn off from the stop-cock. The mass of vapour M, which would saturate this volume at the temperature of the external atmosphere, may be obtained by the aid of the table on p. 241. Finally the hygrometric state of the atmosphere is equal to

$$\frac{m}{M}.$$

For accurate work, however, corrections are necessary, due to the following causes:—

1. The air contained in A at the end of the experiment will generally be at a different temperature from the external atmosphere.

2. The air in A will be saturated with moisture; hence its volume will be different from that which it occupied when in the state of partial saturation pertaining to the external atmosphere.

Vapour Densities.—By the density of a substance is strictly meant the mass of unit volume of that substance. In the case of gases and vapours, however, the term density is often understood to imply the ratio:—

$$\frac{\text{Mass of a certain volume of the gas or vapour at a temperature } t \text{ and pressure } p.}{\text{Mass of an equal volume of dry air at the same temperature and pressure.}}$$

Different methods must be used according as it is required to determine the density of an unsaturated or a saturated vapour.

Density of an Unsaturated Vapour. Gay-Lussac's Method.—Gay-Lussac introduced a small stoppered bottle, filled with a weighed quantity of the liquid to be experimented with, beneath the lower end of a barometer tube. When released, the bottle floated up into the vacuum at the top of the tube. This space was kept at a constant temperature, higher than the boiling point of the liquid, by means of a water-jacket. The stopper of the bottle was forced out by the expansion of the liquid; complete vaporisation then quickly occurred. The volume occupied by the known mass of the substance, in the state of unsaturated vapour, under a pressure deduced from the height of the mercury column and the barometric pressure, thus became known. The mass of a given volume of dry air being known, the vapour density as above defined could be easily calculated.

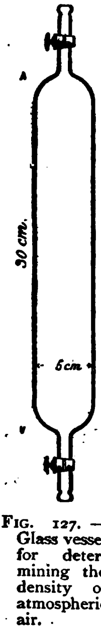

FIG. 127. — Glass vessel for determining the density of atmospheric air.

EXPT. 61.—*To determine the density (mass of unit volume) of dry air.*

Take a cylindrical glass vessel with thick walls, of about the dimensions given in Fig. 127, and provided, as there shown, with a glass tap at each end. Clean this out, and dry it by drawing air through it whilst it is gently heated. Then connect one end with a drying tube, such as that used in the experiment described on p. 246, and the other end with an air pump. Draw air gently through it for about ten minutes. Then close the stop-cock nearest to the pump, and after about a five minutes' interval, allowed in order that the tube and its contained air may attain the temperature of the surrounding atmosphere, close the other stop-cock; observe the temperature of the atmosphere in the room and the barometric pressure. Then disconnect the tube, and weigh it and its contained air.

Once more connect one end of the tube with the air pump, and having opened the appropriate stop-cock, exhaust the tube as completely as possible. When this has been done, close the stop-cock, and weigh the exhausted tube. The difference between this latter weighing and the one previously obtained will give you the mass of the air you have pumped out.

In order to determine the volume of the air you have pumped out, open one of the stop-cocks whilst its nozzle is under water. Water will be forced into the tube by the pressure of the atmosphere, and if the temperature of the water is equal to that of the air, and you immerse the tube so far that the water surfaces are level inside and outside, and then close the stop-cock, the volume of the air previously pumped out will be equal to the volume of the enclosed water. Dry the outside of the tube and weigh it. Subtracting the mass of the tube when exhausted from its mass when partially filled with water, the mass, and thence the volume of the water, is obtained.

The density of the dry air is obtained by dividing its mass by its volume.

Dumas' Method of Determining the Density of an Unsaturated Vapour.—A large glass flask (Fig. 128), provided with a neck drawn out to a fine tube, was partially filled with the liquid the vapour density of which was required, and then immersed in a bath of oil or molten metal which could be maintained at a temperature considerably above the boiling point of the liquid. In order to keep the flask immersed, it was held in a heavy metal frame, which also supported thermometers to indicate the temperature of the bath.

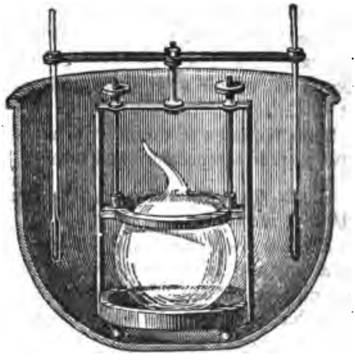

FIG. 128.—Dumas' apparatus for determining the density of an unsaturated vapour.

During the ebullition of the liquid in the flask, the vapour formed issued in a small jet from the drawn out neck. This continued until the liquid was completely vaporised, at which instant the issue of the vapour abruptly ceased. The flask was then full of vapour at the atmospheric pressure and the temperature of the bath. The barometer was then read, and the mouth of the flask was sealed up with a blowpipe.

On weighing the flask a value w was obtained which represented the difference between the mass of the glass vessel plus the contained vapour and the mass of the air displaced. Thus

$$w = w_f + w_v - w_a,$$

if w_f = mass of empty flask weighed *in vacuo*.
w_v = true mass of the contained vapour.
w_a = mass of air displaced by the closed flask.

The flask had previously been weighed with its mouth open to the atmosphere. If w_1 was the value so obtained, we have

$$w_1 = w_f - w'_a$$

where w'_a represents the mass of the air displaced by the glass composing the flask (not that displaced by the closed flask).

$$\therefore\ w - w_1 = w_v - (w_a - w'_a).$$

The quantity within the brackets represents the mass of air at the temperature and pressure of the atmosphere at the time of the experiment which would just fill the flask.

The cubical contents of the flask at 0° C. having been determined, the value of $(w_a - w'_a)$ was calculated from the coefficients of cubical expansion of air and glass, and the density of the atmospheric air at 0° C.

Thus the mass of vapour which filled the flask of known capacity at an observed temperature and pressure was obtained.

EXPT. 62.—*To determine the density of ether vapour by Victor Meyer's method.*

A glass vessel, consisting of a cylindrical bulb A (Fig. 129) joined to a long and rather narrow stem BC, provided with a ground stopper D and a side tube CE, is required for this experiment. The tube and bulb having being cleaned and dried, a small quantity of asbestos fibre or glass wool is pushed down to the bottom of A. The glass vessel is then supported in the manner indicated in the diagram, with the bulb and stem surrounded by a larger glass vessel G containing water, into which a few pieces of capillary tube or porous earthenware have been dropped. The orifice of the side tube is just immersed below the surface of some water contained in a suitable vessel. The stopper D is removed, and the water in the outer vessel is boiled. A small stoppered glass bottle is weighed when empty, and then filled with ether and again weighed. A graduated glass vessel filled with water is inverted over the orifice of the side tube CE, after the manner of a barometer tube. Then the stoppered bottle is dropped down the tube CB into A, the asbestos or glass wool preventing a breakage from occurring, and the orifice D is immediately closed. The stopper is almost immediately forced out of the little bottle, and the ether is quickly vaporised. The vapour formed forces the air in the tube BC before it, and this air collects in the graduated vessel V. The volume of the air collected in V, when corrected for temperature and pressure (p. 231), will be equal to the volume of the ether vapour at 100° C., and the barometric pressure at the time of the experiment. Thus, both the mass and volume of the ether vapour become known, and the density (mass of unit volume) of ether vapour at the atmospheric pressure, and a temperature of 100°, can be directly calculated.

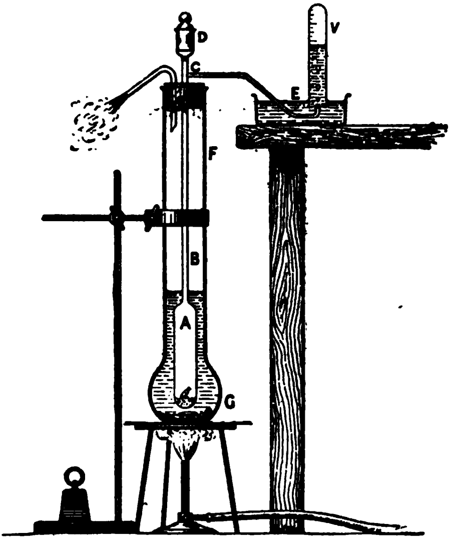

FIG. 129.—Victor Meyer's apparatus for determining the density of an unsaturated vapour.

Density of Saturated Vapours.—The methods previously described are unsuitable for the determination of the density of saturated vapours, since, if the bath were kept just at the boiling point of the liquid, it would be very difficult to seize the exact instant when the whole of the latter had become vaporised. Hence it has been found necessary to employ different methods in this connection.

Fairbairn and Tate's Experiments.—For determining the density of saturated vapours, Fairbairn and Tate used an ingenious method, the principle of which may be understood from the following:—

Let us suppose that a certain weighed quantity of liquid is placed in a closed vessel surrounded by a bath, the temperature of which can be accurately determined. As the temperature of the bath is raised, more and more of the liquid will be evaporated, until at a certain temperature the vessel will be entirely filled with saturated vapour, all of the liquid having disappeared. If there was initially a sufficient quantity of liquid in the vessel, the surface of the liquid will remain visible till the critical temperature is reached; but if only a small quantity of liquid was used, this will only suffice to saturate the space enclosed by the vessel at lower temperatures. Regnault has determined the pressure of saturated vapours at various temperatures; hence, if it were found possible to determine at what temperature the last trace of the liquid was vaporised, we should know the mass of the saturated vapour, and the volume which it occupied, and its pressure could be determined from a knowledge of the temperature of the bath, by the aid of Regnault's tables.

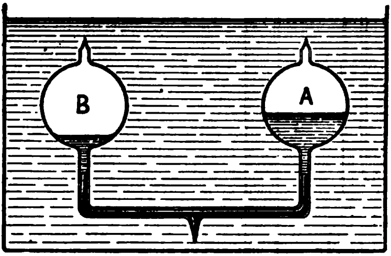

FIG. 130.—Illustrates Fairbairn and Tate s method of determining the density of a saturated vapour.

Eye observations of the amount of liquid left unvaporised at any particular temperature are not sufficiently trustworthy for the requirements of this experiment, as the presence of a small undetected drop of liquid would throw the final results considerably out. On referring, however, to Andrews's curves for carbon-dioxide (Fig. 96, p. 207) an important difference between the behaviour of saturated and unsaturated vapours may be noticed. Draw a vertical line intersecting that part of the isothermals representing the relation between the pressure and volume of the unsaturated vapour. Then the distance measured along this line between any two isothermals will be equal to the increase in pressure when the unsaturated vapour is heated from the temperature of the lower to that of the higher isothermal. On the other hand, the vertical distance between the horizontal parts of the same two isothermals represents the increase in pressure of the saturated vapour between the same limits of temperature.

It will at once be noticed that the increase of pressure of the saturated vapour is much greater than that produced by a similar rise of temperature in the unsaturated vapour. Hence the moment that the whole of the liquid in a closed vessel is evaporated, a falling off will be observed in the rate of increase of the vapour pressure as the temperature of the bath is raised.

Let us now suppose that we are provided with a couple of glass vessels A, B, connected by means of a tube bent twice at right angles (Fig. 130). If the interior of this piece of apparatus is exhausted, and then mercury is introduced into the bent tube, the surfaces will stand at the same level. If, now, different quantities of any one liquid are introduced into A and B, the level of the mercury surfaces will remain undisturbed, except in so far as the pressure due to the head of liquid in one tube may differ from that in the other. The pressure in both A and B will be that due to the saturated vapour of the same substance, and this varies only with the temperature.

On the other hand, if the whole arrangement is placed in a bath which is gradually heated, a difference in the mercury levels will take place directly after the whole of the liquid in one bulb becomes vaporised, provided that some liquid remains in the other.

If the volume of the bulb containing the smaller (weighed) quantity of liquid is accurately known, and the temperature of the bath is noted at the instant when a difference in the levels of the mercury surfaces becomes apparent, we possess all the data requisite for calculating the density of the saturated vapour at that particular temperature. By using greater or smaller quantities of the liquid, higher or lower temperatures will be necessary to entirely vaporise it in the closed space.

Fairbairn and Tait's results are not quite trustworthy, since condensation occurs on the walls of the vessels. Better results are obtained by indirect methods (see Callendar, *Proc. Roy. Soc.*, vol. 67, 1900).

Specific Volume.—By the specific volume of a substance, we mean the volume occupied by unit mass (one gram or one pound) of that substance.

Fig. 131 represents the general form of the isothermal of a substance, at and below the critical temperature. The substance will be wholly in a state of saturated vapour only at the extremities A, B, C of the straight portions AD, BE, CF of the respective isothermals. Hence in order that the specific volume of the saturated vapour at various temperatures should be determined, the substance must be constrained to pass through the conditions corresponding to the dotted line ABCK. If the curves (Fig. 131) refer to one gram of a substance, then its specific volume at the temperatures corresponding to the different isothermals will be given by O*a*, O*b*, O*c*, O*k*.

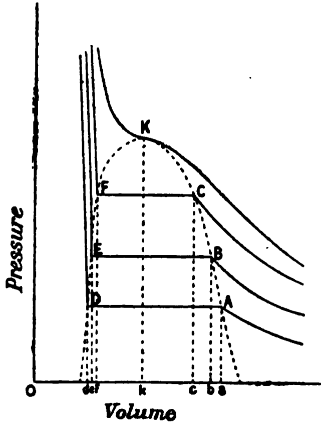

FIG. 131.—Isothermals of a substance for temperature below the critical temperature, indicating the variations in the specific volume of the liquid and saturated vapour with temperature.

Similarly, it may be shown that the specific volumes of the liquid substance will be equal to O*d*, O*e*, O*f*, and O*k*. It will at once be seen that while the specific volume of the liquid increases with the temperature, the specific volume of the saturated vapour decreases with the temperature. At the critical temperature, the specific volumes of both the liquid and saturated vapour have the same value, viz., O*k*. Further, the specific volume varies most quickly in the neighbourhood of the critical temperature, both in the case of the solid and of the liquid.

The specific volumes of liquid hydrochloric acid and its saturated vapour, are graphically represented in Fig. 132. These curves are due to Mr. G. Ansdell. It will be seen that the liquid and saturated vapour curves join each other at K. This point corresponds to the critical temperature of hydrochloric acid.

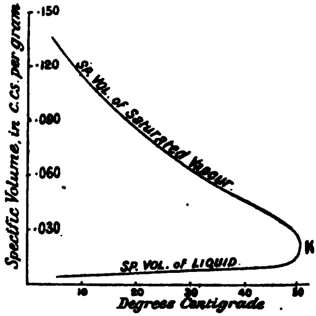

FIG. 132.—Specific volume of hydrochloric acid (after Ansdell).

SUMMARY

Vapour Pressure.—When a quantity of a liquid or solid is placed in an otherwise empty enclosure, part of the substance evaporates, and the vapour thus formed exerts a definite pressure. This pressure depends only on the temperature and not on the volume of the enclosure. If the volume of the enclosure is diminished, part of the vapour is condensed, and the remainder exerts the same pressure as previously. If different parts of the enclosure are at different temperatures the vapour pressure will correspond to the coldest part of the enclosure.

Regnault has determined the vapour pressure of a number of substances at various temperatures. Consequently a measurement of the vapour pressure of one of these substances suffices to determine its temperature.

The pressure of a mixture of gas and vapour is equal to the sum of the pressures of the gas and the vapour for the given volume and temperature. (Dalton's Law.)

The vapour pressure of a solution of a non-volatile substance in water or any other pure liquid is always lower than the vapour pressure of the solvent at the same temperature. The amount by which the vapour pressure is lowered is proportional to the number of dissolved molecules. Substances which form electrically conducting solutions appear to be dissociated.

The Triple Point.—If curves be drawn representing for a substance the relation (1) between temperature and vapour pressure of the liquid, (2) temperature and vapour pressure of the solid, and (3) the variation of the melting point with pressure, these three curves will meet in a point. This point is termed the triple point. At the temperature and pressure corresponding to this point, the substance may simultaneously exist in equilibrium in the states of solid, liquid and vapour. At the temperature corresponding to the triple point, the substance may boil and freeze simultaneously.

The isothermals of a substance for the states of solid, liquid, and vapour will have different forms according as the substance contracts or expands on solidifying.

Hygrometers.—An instrument designed to determine the amount of aqueous vapour in a given volume of atmospheric air is termed a hygrometer.

The hygrometric state of the atmosphere is measured by the ratio

$$\frac{\text{Mass of aqueous vapour in 1 c.c. of air at the observed temperature}}{\text{Mass of aqueous vapour necessary to saturate 1 c.c. of air at that temperature.}}$$

Dew Point.—The temperature at which the aqueous vapour, actually existing in a given volume of atmospheric air, would suffice to saturate that volume is called the dew point.

Dew Point Hygrometers.—In these instruments a surface is cooled down gradually till the deposition of dew commences, when the temperature of the surface is observed. The hygrometric state of the atmosphere can then be determined by reference to tables.

In the **chemical hygrometer** the aqueous vapour in a certain volume of air is absorbed by a suitable chemical substance, such as phosphorus pentoxide or strong sulphuric acid. The mass of vapour absorbed is determined by weighing.

The wet and dry bulb hygrometer consists of two thermometers, the bulb of one being covered with muslin moistened with water. The rate at which water evaporates from the wet bulb depends on the hygrometric state of the atmosphere.

Vapour Densities.—The density of a vapour may be measured either as the mass of unit volume of the vapour, or as the ratio of the mass of a certain volume of the vapour at a particular temperature, to the mass of an equal volume of dry air, at the same temperature and standard atmospheric pressure.

Gay-Lussac determined the density of unsaturated vapours by observing the volume which a known mass of the vapour occupied when introduced into the space at the top of a barometer tube.

Dumas determined the density of unsaturated vapours by filling a bulb of known volume with the vapour, and then weighing.

Density of Saturated Vapours.—*Fairbairn and Tate's experiment.* The fact that the pressure of a saturated vapour increases more rapidly with the temperature than the pressure of an unsaturated vapour, can be seen by referring to Andrews's curves for carbon dioxide. This fact was utilised by Fairbairn and Tate to determine the instant at which a weighed mass of liquid had been entirely converted into saturated vapour, filling a known volume.

The specific volume is the volume of unit mass of a substance.

The specific volume of a liquid increases with the temperature.

The specific volume of a saturated vapour decreases with the temperature.

At the critical point the specific volume of a liquid and its saturated vapour are equal.

QUESTIONS ON CHAPTER X.

(1) Explain a method of measuring the vapour pressure of a liquid at relatively high temperatures.

(2) Define the hygrometric state of the atmosphere, and explain how it may be determined.

(3) What is meant by an isothermal curve? Indicate the form of such a curve (*a*) for a gas, (*b*) for a vapour. How is the work done in compressing the gas or vapour shown on the indicator diagram? (For last part of question, *see* Chap. XVII.)

(4) What do you understand by an isothermal curve? Indicate the form of such a curve (*a*) for a mass of dry gas at 15°, (*b*) for the same gas when saturated with water vapour.

(5) Describe some method of measuring accurately the vapour pressure of a liquid at various temperatures.

(6) Define the triple point. Draw figures showing the three lines which meet in the point (1) when the solid is less dense; (2) when it is more dense than the liquid at the same temperature and pressure. Indicate clearly in each case what parts of the diagram are allotted to each of the three states.

(7) Define the dew point, and explain how to find the mass of aqueous vapour present in a given volume of air.

(8) Distinguish between a gas and a vapour. How would you show that the pressure of a mixture of gases and vapours between which there is no chemical action is equal to the sum of the pressures which each would severally exert if alone present?

(9) Two liquids, A and B, are introduced into two barometer tubes, the temperature of each being the same. It is noticed (1) that in both cases a little of the liquid does not evaporate; (2) that the mercury in the tube containing A is more depressed than that in the tube into which B was introduced. Which liquid would you expect to have the higher boiling point? Give reasons for your answer.

(10) What is the meaning of the term "Humidity," or "Hygrometric state," as applied to the atmosphere? Give a short description of the instruments that are commonly employed for finding the state of the air with respect to moisture. The dew point on a certain day being found to be 12° C., and the temperature of the air being 16·5° C., find its humidity, given that the maximum pressure of aqueous vapour at 12° is equivalent to 1·046 cm. of mercury, while that at 16° is 1·364 cm., and that at 17° is 1·442 cm.

(11) What is meant by the maximum vapour pressure of a liquid at a given temperature? Describe a method by which it has been measured for water.

(12) How would you experimentally determine the vapour tension of alcohol at different temperatures?

(13) Define the hoar-frost line, the ice line, and the steam line. Show that they meet at a point, and how to calculate the angles at which they meet.

(14) Give an account of the deviations from Boyle's Law exhibited by different gases. Assuming Boyle's Law to hold, find the weight of

dry air in a vessel containing 300 c.cs. of air saturated with aqueous vapour at 20° C. and subject to a total pressure of 73·74 cms. of mercury; the density of air at 0° and 76 cms. being 0·001293 gr./c.c., and the pressure of aqueous vapour at 20° being 1·74 cm. of mercury.

(15) State Dalton's laws of vapours.

On a day when the barometer is 760 mms. high, the temperature of the air is 20° C., and the relative humidity is 0·5; what fraction of the whole pressure of the air is due to water vapour? The saturation pressure at 20° is 18 mms.

(16) Distinguish between saturated and non-saturated vapours.

Describe some form of hygrometer, and point out any defects in the instrument described.

(17) A mixture of air and of the vapour of a liquid in contact with excess of the liquid is contained in a vessel of constant volume. At a temperature of 15° C. the pressure in the vessel is 70 cms. of mercury, at 30° C. it is 88 cms., at 45° it is 110 cms., and at 60° it is 145 cms. Assuming that at 15° C. the vapour pressure of the liquid is 15·4 cms., calculate the vapour pressure at 30°, 45°, and 60° C.

(18) A body expands on solidifying. Draw and explain the isothermal curve for a temperature at which the body can exist (under proper conditions of pressure) in the solid, liquid and gaseous state.

PRACTICAL.

(1) Find the dew point by a Regnault hygrometer, and calculate the density of the air at the place of experiment (density of dry air at 0° and 760 mms. = 0·001293, density of water-vapour = $\frac{5}{8}$ density of dry air).

(2) Determine the dew point, and deduce by the aid of tables the weight of water in a litre of the air of the room.

(3) Find the vapour pressure of water from 80° to 100°.

(4) Measure the vapour pressure of the air in the laboratory by means of a chemical hygrometer.

CHAPTER XI

MECHANICAL CONSIDERATIONS

IN the ensuing chapters, attention will be directed to the connection between heat and mechanical work. As a preliminary, a short sketch will here be given of some of the most important principles of mechanics. We will commence with a consideration of the units of measurement.

Primary Units. *Length.*—The scientific unit of length is the *centimetre*, being one hundredth part of the distance (one metre) between two marks on a platinum bar, preserved at Paris. The *metre* was originally defined as one ten-millionth of an earth quadrant ; *i.e.* one ten-millionth of the distance, measured along a meridian on the surface of the earth, from the pole to the equator. This definition is, however, of little importance ; the metre may be taken as an arbitrary length defined by the distance between two marks on the standard bar mentioned above.

The English unit of length is the *foot*.

Mass.—The scientific unit of mass is the *gram*, and is defined as the mass of one cubic centimetre of pure water, at the temperature of its maximum density, *i.e.*, 4° C. For many purposes it is sufficiently accurate to take the gram as the mass of 1 c.c. of water, irrespective of the temperature.

The English unit of mass is the *pound*.

Time.—The scientific unit of time is the *second*. It is primarily defined from astronomical data which will not be considered here. For ordinary physical (as distinguished from astronomical) calculations, time may be measured by an ordinarily good watch.

Derived Units. *Velocity.*—When a body is moving uniformly (*i.e.*, so that in equal intervals of time it passes over equal distances in the same direction), the velocity is measured by the distance traversed in one second.

If the body moves uniformly through x centimetres during t seconds, then its velocity will obviously be equal to $\frac{x}{t}$ cms. per second.

The velocity of a body may vary as follows :—

(1) It may vary in magnitude, remaining constant in direction.

Example. A stone falling towards the earth.

(2) It may remain constant in magnitude, but vary in direction.

Example. The motion of any given portion of the rim of a wheel, which is revolving uniformly.

(3) Both of these variations may occur simultaneously.

Example. The motion of the bob of a pendulum.

Instantaneous Velocity.—The velocity of a body which is not moving uniformly is measured as follows. Let dx be the distance through which the body moves, in a time dt so short that the velocity may be considered to have remained constant during that interval. Then the velocity of the body, at the instant under consideration, $= \frac{dx}{dt}$.

The notation here used is that of the differential calculus, but no knowledge of that branch of mathematics is presupposed on the part of the student ; dx must be taken, *as a whole*, to mean a very short distance by which x is increased in a very small time dt. Thus dx does *not* mean $d \times x$; and similarly with dt.

We might define the velocity of a body at any instant as the distance through which the body would travel in one second, if it continued moving as at the instant under consideration.

Acceleration.—The rate of change in the velocity of a body is termed its acceleration.

If a body, initially at rest, is found, after an interval of one second, to be moving with unit velocity (*i.e.*, 1 cm. per second), then the acceleration is equal to one centimetre per second in a second, or 1 cm./sec.^{2}

Generally, if the velocity of a body, at a certain time t, is equal to v cms. per second, whilst at a time $t + dt$ the velocity has increased to $v + dv$ cms. per second, then the acceleration is equal to $\frac{dv}{dt}$.

Force.—According to the system of mechanics introduced by Newton, the velocity of a body cannot be altered without the application of a force. In other words, force is that which changes, or tends to change, the velocity of a body.

Newton's first law of motion may be stated as follows :—

A body will continue at rest, or moving uniformly in a straight line, unless acted on by an extraneous force.

The Unit of Force, called the Dyne, may be thus defined :—*If a mass of one gram is acted on by unit force, then the velocity of the body will increase at the rate of one cm. per second in each second.*

The method by which this unit is introduced into calculations will be made clearer by an example.

A body, of which the mass is one gram, is allowed to fall from rest under the action of gravity. What distance will the body describe in t seconds?

Let g = the acceleration due to gravity, *i.e.*, the force exerted by gravity on a mass of one gram ; then, according to the definition just given, this force acting on a gram would communicate to it a velocity of g cms. per second at the end of one second ; $2g$ cms. per second at the end of two seconds ; and tg cms. per second at the end of t seconds. But the average velocity of the body during these t seconds would be

$$\frac{0 + tg}{2} = \frac{tg}{2} \text{ cms. per second.}$$

Since the body has been moving with this average velocity during t seconds, it will have moved through $t \times \frac{tg}{2} = \frac{1}{2}gt^2$ cms. in that time.

Statical experiments show that gravity exerts on two grams of matter a force twice as great as that on one gram. Further, a well-known experiment shows that a guinea and a feather fall at the same rate when in a vacuum. That is to say, after t seconds a feather will have acquired the same velocity as a guinea, if both fall from rest in a vacuum. Now, m grams will be acted on by a force mg, but this force has to move m grams of matter. In order that the velocity acquired in t seconds should be independent of m, we must assume that *the velocity generated in m grams of matter by a given force, f, is $\frac{1}{m}$ of that which would have been produced by the same force acting on one gram of matter.*

Thus, force of gravity acting on m grams $= mg$ dynes. Velocity generated by this force during t seconds $= \frac{mgt}{m} = gt$.

Let a = the acceleration (rate of change of velocity) of a body. If the mass of the body were equal to 1 gram, the force acting on the body would, by definition, be equal to a dynes. If the mass of the body is equal to m grams, then the force must be equal to ma dynes. In other words, force = mass × rate of change of velocity.

Momentum.—*The product of the mass of a body into the velocity with which it is moving, is called the momentum of the body.*

Let m be the mass, and v the instantaneous velocity of a body.

Then, force acting on body $= m \times$ rate of change in v. But since the mass of the body is constant, we may write force = rate of change in (mv) = rate of change of momentum.

Example. A mass of M_1 grams is attached, by means of a flexible and inextensible cord passing over a frictionless pulley, to a mass of M_2 grams lying on a perfectly smooth table. (M_2 can thus move over the table without any frictional force being exerted.) With what velocity will the masses be moving after t seconds if, when the cord is tight, M_1 is allowed to fall from rest?

$$\text{Force on } M_1 = M_1 g \text{ dynes.}$$

This force would produce a velocity of M_1gt cms. per second at the end of t seconds if acting only on one gram. But both masses must move with the same velocity, and hence the above force must move $(M_1 + M_2)$ grams.

$$\therefore \text{ Velocity generated in } t \text{ seconds} = \frac{M_1gt}{M_1+M_2}.$$

Space moved through by either weight in t seconds =

$$\tfrac{1}{2} \cdot \frac{M_1gt}{M_1+M_2} \cdot t = \tfrac{1}{2} \frac{M_1gt^2}{M_1+M_2}.$$

Example. Two bodies of masses equal to M_1 and M_2 (where $M_1 > M_2$) are hung by an inextensible and flexible cord over a frictionless pulley. What will be the velocity of either body after t seconds, and what space will it have described?

Force of gravity acting directly on $M_1 = M_1g$ dynes.
,, ,, ,, $M_2 = M_2g$,,

But the force acting directly on either body is transmitted by means of the cord to the other body. Hence resultant force on $M_1 = M_1g - M_2g$ acting downwards.

Resultant force on $M_2 = (M_2g - M_1g)$ acting downwards, or $(M_1 - M_2)g$ acting upwards.

Hence the force $(M_1 - M_2)g$ has to move $M_1 + M_2$ grams of matter.

Therefore velocity of either body after t seconds =

$$\frac{(M_1 - M_2)gt}{M_1 + M_2} \text{ cms. per second.}$$

Space covered by either in t seconds.

$$\frac{1}{2}\frac{(M_1 - M_2)t^2}{M_1 + M_2} \text{ cm.}$$

Work and Energy.—*When a body, acted on by any forces, is moved from one position to another, the product of the component force opposing its motion, into the distance through which the body is moved, is defined as the work performed on the body.*

Unit of Work.—*The work performed when a force of* 1 *dyne is overcome through a distance of* 1 *cm. is called an* erg.

When a force of f dynes is overcome through a distance of d cms., the work performed will be equal to fd ergs.

Let us apply this definition to the case of a body of mass m, raised, against gravity, through a vertical distance of h cms. The force acting on the body = Mg, where g, as previously defined, has a value of about 981 cms. per second per second. Hence work performed = Mgh. The body is said to possess, at this second position, an amount of **potential energy** = Mgh ergs, with respect to its initial position; or, otherwise stated, the potential energy of a body of mass M is increased by Mgh ergs, when it is raised through a distance of h cms. against the force of gravity.

Now let the body fall freely. When it reaches its initial position, it will have fallen through a distance $h = \frac{1}{2}gt^2$, where t is the time taken in falling. But the velocity, v, of the body after this interval = gt. Hence, since $v^2 = (gt)^2 = g \times gt^2 = 2gh$, we have the following relation

$$Mgh = \frac{1}{2}Mv^2.$$

This is a most important relation, and its meaning should be carefully studied. The left-hand side of the equation is equal to the work performed in moving a body from one point to another, through a distance h, against a force equal to Mg which, if unopposed, would cause the body to move in the opposite direction ; in other words, it represents the difference in the potential energies possessed by the body at the two points. The right-hand side of the equation represents a function of the mass and velocity of the body, to which the term *Kinetic Energy* is applied. The above equation may therefore be expressed in words as follows :—

The kinetic energy which a body will acquire in falling freely from one position to another, is equal to the difference between the potential energies possessed by the body at those positions.

In defining the work performed in moving a body from one position to another, as equal to the product of the force resisting the motion of the body, into the distance through which it is moved, nothing is said about the force which produces the motion of the body. This must of necessity be slightly greater than the resisting force, otherwise the body would not begin to move.

Now we may define the product of the force exerted on the body by an external agent, into the distance through which the body is thereby caused to move, as the work performed *by the agent.*

If the work performed *on a body* when it is moved through any distance against a resisting force is taken to be positive, the work performed *by an agent*, as defined above, may be given a negative sign. In one case the force and the distance moved through have opposite signs, whilst in the other case the signs are similar.

If the force exerted by the agent in moving a body is uniformly greater than the force resisting this motion, the excess of the work performed by the agent, over the work performed on the body, will be spent in communicating kinetic energy to the body. Thus, if $F =$ the force exerted by the agent, $f =$ the force resisting the motion of the body, $h =$ the distance moved through, and $M =$ the mass of the body, supposed to be initially at rest, then the velocity of the body after having been moved through the h cms. is given by v in the equation

$$Fh = fh + \tfrac{1}{2}Mv^2.$$

Units of Work.—The following units of work are used:—

An erg is the work performed in overcoming a force, equal to 1 dyne, through a distance of 1 centimetre.

A centimetre-gram is the work performed in overcoming a force equal to that exerted by gravity, at a particular place, on a mass of 1 gram, through a distance of 1 cm. At places where $g = 981$, 1 centimetre-gram = 981 ergs.

A metre-kilogram is the work performed in overcoming a force equal to that exerted by gravity on a mass of 1 kilogram (1,000 grams), through a distance of 1 metre (100 cms.). If $g = 981$,

$$1 \text{ metre-kilogram} = 1{,}000 \times 981 \times 100 = 9{\cdot}81 \times 10^7 \text{ ergs.}$$

A foot-pound is the work performed in overcoming a force equal to that exerted by gravity on a mass of 1 pound through a distance of 1 foot.

Taking 1 inch = 2·54 cms., 1 lb. = 453·6 grams, it may be seen that

$$1 \text{ ft.-lb.} = 453{\cdot}6 \times 981 \times 12 \times 2{\cdot}54 = 1{\cdot}337 \times 10^7 \text{ ergs.}$$

A foot-poundal is the work performed in overcoming a force of 1 poundal through 1 foot.

$$1 \text{ ft.-lb.} = 32 \text{ ft.-poundals.}$$

When kinetic energy is expressed by

$$E = \tfrac{1}{2} Mv^2,$$

the result will be measured in *ft.-poundals* or in *ergs*, according as the English or the metric system is used.

Kinetic energy, measured in ft.-lbs. $= \dfrac{\frac{1}{2}Mv^2}{g}$.

M is measured in lbs., v in ft. per second, and $g = 32$ ft./sec.^{2}

Power is defined as rate of performing work. If 33,000 ft.-lbs. of work are performed in one minute, then the rate of performance of work is defined as **one horse-power**.

In the C.G.S. (centimetre, gram, second) system, the unit of power is one erg per second.

One watt = 10^7 ergs per second. One horse-power = 746 watts.

SUMMARY

The velocity of a body at any instant is defined as the distance through which the body would travel in one second, if it continued moving as at the instant under consideration.

Acceleration.—The rate of change in the velocity of a body is termed its acceleration.

Momentum.—The product of the mass of a body into the velocity with which it is moving at any instant is defined as the momentum of the body at that instant.

The resultant force acting on a body is measured by the rate of change of the momentum of the body.

The dyne is the unit of force in the C.G.S. (centimetre, gram, second) system. This force would increase the velocity of one gram of matter by one centimetre per second in each second.

The poundal is the unit of force in the English system. It would increase the velocity of one pound of matter by one foot per second in each second.

Force of gravity on one gram of matter = 981 dynes.

Force of gravity on one pound of matter = 32 poundals.

Work is measured by the product of the force opposing the motion of a body into the distance, parallel to that force, through which the body is moved.

An erg of work is performed when a body is moved through one centimetre against a force of one dyne.

A foot poundal of work is performed when a body is moved through one foot against a force of one poundal.

A foot-pound of work is performed when one pound is raised against the force of gravity through a distance of one foot.

Kinetic Energy is the name given to the product of half the mass of a body into the square of the velocity with which the body is moving, Or, kinetic energy = $\frac{1}{2}Mv^2$.

Potential Energy.—When work is performed in moving a body from one position to another, against a force which would cause the body to move in the opposite direction if alone acting on it, the potential energy of the body is said to be increased by a quantity equal to the work performed.

QUESTIONS ON CHAPTER XI.

(1) Define the terms energy and work, and explain how, first, the kinetic, secondly, the potential, energy of a falling body is measured.

(2) What is meant by energy of position, and by a foot-pound?

A reservoir of water, of area 330,000 sq. feet, is initially of uniform depth 10 feet. How many ft.-lbs. can it supply to a turbine on a level with the bottom of the reservoir, and what horse-power can it maintain on the average if it is emptied in 10 hours?

1 cubic ft. of water weighs 62·4 lbs; 1 horse-power is 33,000 ft.-lbs. per minute.

CHAPTER XII

THE FIRST LAW OF THERMODYNAMICS

Theories of Heat.—In the earlier theories, heat was considered to be an elastic fluid which material bodies could, so to speak, absorb, their temperatures being thereby raised. This explanation is tolerably sufficient as far as calorimetric experiments are concerned, although we have already had occasion to remark that a very different conception will simplify the explanation of many interesting phenomena. It now, however, becomes necessary to inquire more carefully into the nature of heat.

Curiously enough, an experiment with which savage tribes are familiar throws a flood of light on the subject. That two bodies when rubbed together become warmer is a phenomenon with which every one is familiar. Savages manage to obtain a sufficient rise of temperature, by rubbing two pieces of wood together, to produce ignition. Now this means that, during the rubbing, a certain quantity of heat has made its appearance; and unless we assume that the heat is squeezed out of one of the bodies, much as water may be squeezed out of a sponge, it becomes difficult to account for such a phenomenon.

Francis Bacon, Baron Verulam, seems to have been the first to attempt a systematic examination of the various facts known in regard to heat, in order to form a rational theory by which the facts might be explained. After carefully considering a large number of mechanical methods by which heat could be produced, he reached the conclusion that heat is inseparably connected with motion.

Caloric.—Up to the beginning of the present century, philosophers for the most part considered heat to consist of an elastic fluid, which they termed *caloric*. In order to account for the flow of heat from hot to cold bodies when placed in contact, this fluid was supposed to possess the property, that different parts of it repelled each other. To account for the difference in the specific heats of different bodies, matter was supposed to possess an attraction for caloric, which varied with the chemical constitution of the body. Further, caloric was considered to be indestructible. Hence, caloric lost by one body was always gained by some other body or bodies. As to whether caloric possessed weight, opinions were divided, till in 1799 Count Rumford performed a series of delicate experiments, leading to the conclusion that "all attempts to discover any effect of heat upon the weights of bodies will be fruitless."

Certain philosophers considered that it was necessary to assume the existence of other elastic fluids, similar in many respects to caloric, but differing in their mechanical and thermal effects on bodies. Thus, the expansion of ice on freezing was by some accounted for by assuming the introduction of a fluid termed *frigorific*.

Heat produced by the Compression of a Gas.—Every one who has inflated a bicycle tyre will probably have noticed that the end of the pump nearest to the tyre becomes heated during the operation. In this case, heat is produced by the compression of the air in the pump. That heat is produced during the compression of a gas was first noticed by Dr. Cullen and Dr. Darwin.

The Fire Syringe.—This instrument consists of a cylindrical glass tube closed at one end, and fitted with an air-tight piston. In order to exhibit the effect of the heat produced when the contained air is compressed, a piece of cotton-wool moistened with carbon bisulphide is thrown into the tube and then removed. By this means the tube is left filled with a mixture of air and carbon bisulphide vapour. On suddenly pressing the piston inwards, this mixture is compressed, and the flash of light which is seen indicates that a sufficiently high temperature has been attained to ignite the inflammable vapour.

Dalton's Experiments.—Dalton was the first to measure the rise in temperature produced by compressing air. He concluded that when a given quantity of air is compressed to half its volume, a rise of 50° F. (27·8° C.) is produced.

Dulong confirmed this result, and showed that the rise in temperature for a given compression is independent of the nature of the gas experimented on. An expansion of a gas is attended by a corresponding fall in temperature.

Count Rumford's Experiments.—Whilst engaged in superintending the boring of cannon at the naval arsenal at Munich, Count Rumford was impressed by the high temperature of the metallic chips thrown off. The calorists, of course, were familiar with the fact that heat is produced when two bodies are rubbed together; they explained this by stating that during the process, the particles of the bodies are pressed closer to each other and caloric is thus extruded; and, further, that the specific heat of a substance in a state of fine division is less than that of the same substance when in large masses. Neither of these statements appear to have been founded on any special experimental evidence.

To examine the matter further, Rumford mounted a cylindrical mass of gun metal so that it could be rotated by horse-power, and pressed a blunt borer against one of its ends. A flannel covering was provided to prevent loss of heat, whilst a thermometer, placed in a small hole bored for the purpose, served to indicate the temperature of the mass.

After 960 revolutions had been made, it was found that the temperature had risen from 60° F. to 130° F. The metallic dust abraded was found to weigh 837 grains Troy. "Is it possible," he wrote, "that the very considerable quantity of heat produced in this experiment (a quantity which actually raised the temperature of above 113 lbs. of gun metal at least 70 degrees of the Fahrenheit thermometer, and which, of course, would have been capable of melting 6½ lbs. of ice, and of causing near 5 lbs. of ice cold water to boil), could have been furnished by so inconsiderable a quantity of metallic dust, and this merely in consequence of *a change* in its capacity for heat?"

Rumford further convinced himself that the specific heat of the metal employed was sensibly the same, whether that metal was in large masses or in the state of chips. He concluded that there was no reason to suppose that the same metal, when reduced to a state of finer division by the action of a blunt borer, would have its specific heat altered to any great extent.

The most cogent reason urged by Rumford against the calorists, was that there appeared to be *no limit to the amount of heat that could be produced by friction.* Unless a body is considered to initially possess an infinite store of caloric, it would appear rational to suppose that the amount which could be extruded by pressing the particles closer together must be limited. On the other hand, Rumford found that the evolution of heat was as brisk at the end as at the beginning of the experiment.

Rumford also found that if the metal cylinder was immersed in water, the latter could be boiled by the heat produced when the cylinder was rotated with a blunt borer pressed against its end.

"It is hardly necessary to add," Rumford concluded, "that anything which any insulated body or system of bodies can continue to furnish *without limitation* cannot possibly be a *material substance;* and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner the heat was excited and communicated in these experiments, except it be **Motion.**"

Davy's Experiments.—In 1799, Humphry Davy published a work entitled, "Essay on Heat and Light and Combinations of Light," in which the theory of caloric was once for all disproved.

He states that he procured two pieces of ice, and fastened these by the aid of wire to two metal bars. The ends of the two pieces of ice were placed in contact, and rubbed together violently by the aid of suitable mechanism. After a short time nearly all of the ice was melted, and the resulting water was found to have attained a temperature of 35° F.

Further experiments were performed, in which the blocks of ice were rubbed against each other in a vacuum.

Now there is no question that a considerable quantity of heat must be communicated to a mass of ice at 0° C., in order that it may be converted into water at the same temperature. That heat is capable of being squeezed out of the ice, or that the specific heat of water is less than that of ice, are both alike inadmissible explanations of this experiment. Further, the conclusion reached by Davy, that any quantity of ice could be melted by a sufficient amount of rubbing, must be taken to confirm Rumford's statement, that an unlimited supply of heat can be obtained by rubbing two bodies together for a sufficient time. Hence *the idea that heat is a material or quasi-material fluid must be finally abandoned.*

Work and Heat.—Let us, for a moment, consider the experiments of Rumford and Davy from a slightly different standpoint. In both cases bodies pressed against each other were maintained in relative motion, and in both cases the friction between the bodies opposed their relative motions. In other words, the moving body was kept in motion against an opposing force. But this means that work was being performed. The question now naturally arises, is there any relation between the work performed and the heat produced.

This question was for the first time answered in a perfectly satisfactory manner by Dr. Joule, of Manchester, as a result of experiments commenced in 1840.

In 1842, Dr. Julius Robert Mayer, of Heilbronn, stated that there was a strict equivalence between the work performed and the heat produced in any particular circumstances. He even calculated the value of the work which would suffice to raise the temperature of a given quantity of water through a given number of degrees. His conclusions, however, were founded on certain assumptions which have since been proved to be only approximately true, and which were, moreover, not generally accepted at the time when Mayer published his statement. Other physicists had grasped the idea of the equivalence of heat and energy prior to the time at which Joule published the results of his classical researches; but in all of these cases the conviction entertained had more or less of the nature of a plausible assumption, whilst Joule's conclusions were based on experimental evidence of the most conclusive and unimpeachable character.

Before proceeding to consider how the equivalence between energy and heat was proved by Joule, a recently devised experiment, which can be performed by the student himself, will be described. It illustrates the essential principles underlying all such investigations, and suffices to determine the amount of energy equivalent to unit quantity of heat, with an error not exceeding one per cent.

EXPT. 63.—*To determine the amount of energy which is equivalent to unit quantity of heat, using Prof. Callendar's apparatus.*—Let us suppose that a body is pulled along a flat strip of brass which is laid on a table. The motion of the body is opposed by the frictional resistance called into play, and consequently work must be done in moving the body. If it is pulled along the strip by a cord, which passes over a frictionless pulley and is then fastened to a weight which can descend vertically, the work done is equal to the force of gravity acting on this weight, multiplied by the distance through which it descends. Now let us suppose that the strip of brass is pulled along the table in a direction opposite to that in which the body tends to move under the action of the weight; if the speed with which the strip moves is sufficient, the body will remain stationary, the frictional force exerted on it by the moving brass strip being equal and opposite to the pull exerted by the weight. The work done is now equal to the pull of gravity on the weight *multiplied by the distance through which the brass strip is moved.* The heat produced will be distributed in the body and the brass strip, and can be determined if the specific heats of the body and the strip are known, and the rises in their temperature can be observed. However, very little work would be done under the supposed conditions, and the temperatures of the body and the strip could not be observed with accuracy; besides which, much heat would be lost during the experiment. If we imagine the strip to be bent into the form of a circular cylinder, which is rotated about its axis so that the body pressing on its curved surface remains stationary, the same reasoning will apply, but now work can be performed continuously, and the matter which absorbs the heat will be more concentrated, with the result that the heat produced can be measured with accuracy. This will serve to explain the principle on which Prof. Callendar's apparatus is constructed.

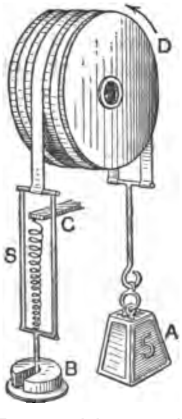

FIG. 133.—Diagrammatic representation of Prof. Callendar's apparatus for determining the work which will produce unit quantity of heat.

The essential parts of this apparatus are represented in Fig. 133. D is a brass drum mounted so that it can be rotated about a horizontal axis coinciding with the axis of the cylinder. A weight, A, of about 3 to 5 kilograms, is hung from two parallel silk ribbons, which are wrapped once round the curved surface of the cylinder, their ends being connected by a cross-piece of ebonite, to the middle of which another silk ribbon is attached; this ribbon also is wrapped round the cylinder, lying between the other two ribbons, and is finally attached to a framework which carries a weight, B, of about 200 to 400 grams. The drum is rotated at the rate of about 60 to 100 revolutions per minute, in the direction of the arrow; the frictional force exerted by the rotating drum on the ribbon serves to support the weight, A, when the ribbon is wrapped tightly enough round the drum. In order to automatically adjust the tension of the ribbon, and with it the frictional force called into play, part of the force exerted by the weight B is taken by a spring balance, S, the upper end of the spring being attached to C, a part of the stand which supports the apparatus. The more the lower end of the spring descends, the more is the spring stretched, and the greater part of the weight B does it take. Let us now suppose that at a particular instant the ribbon is wrapped too tightly round the cylinder; the frictional force will be too great, the weight A will rise, and the end of the ribbon which supports B will descend, with the

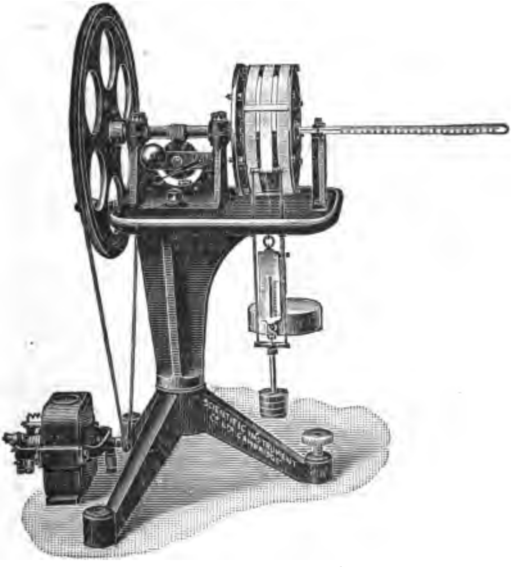

FIG. 133A.—Prof. Callendar's apparatus.
(Supplied by the Cambridge Scientific Instrument Co.)

result that more of the weight B is taken by the spring, and less by the ribbon; hence the ribbon automatically becomes more slack, and the frictional force called into play diminishes.

Let M be the mass of the weight A and the brass hook to which it is attached; and let m_1 be the mass of the weight B and the framework which carries it, while m_2 is the reading[1] of the spring balance, which gives the weight supported by the spring S. Then the force Mg opposes the rotation of the drum, while the force $(m_1 - m_2)g$ assists it; hence the resultant opposing force is equal to $(M - m_1 + m_2)g$, and if this is multiplied by the product of the circumference of the drum and the number of revolutions completed in a given time, we shall obtain the work done in that time.

The drum weighs about 700 grams, and as the specific heat of brass is roughly equal to 0·1, the water equivalent of the drum is about 70 grams. Four hundred and thirty grams of water are introduced into the drum, so that the water equivalent of the drum and its contents is 500 grams. The bulb of a bent thermometer dips into the water, so that the rise of temperature can be accurately observed. The rotation of the drum keeps the water well stirred.

A revolution counter rings a bell at the end of every hundred turns of the drum, and if the thermometer is read every time the bell rings, it will be observed that approximately equal rises of temperature are produced; hence, since the work done in a hundred turns is always the same, equal amounts of work produce equal quantities of heat, or **the work W done is proportional to the heat H produced.** Hence if we divide W by H, we obtain a constant giving the number of units of work which are equivalent to unit quantity of heat. The ratio W/H is called the **mechanical equivalent of heat** or **Joule's equivalent**, and is denoted by J.

An accurate value of J can be obtained by taking the following precaution. To eliminate loss of heat, the initial temperature of the water is made as much below the temperature of the room as the final temperature will be above it.

Joule's Experiment.—The method used by Joule in his determination of the mechanical equivalent of heat is essentially similar to that employed in the foregoing experiment.

A quantity of water was contained in a copper vessel AB, Fig. 135, of peculiar design. This vessel was fitted with a watertight lid, provided with two apertures, a central one through which passed a spindle, and an eccentric one through which a sensitive thermometer could be inserted. The spindle carried eight sets of radial arms, which were so constructed that they could just pass through apertures cut in four radial vanes attached to the inside of the containing vessel. Fig. 134 is reproduced from a photograph of the actual vessel used by Joule; this is now preserved in the science collection at South Kensington Museum.

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[1] An index shows the weight supported by the spring balance; this is not shown in Fig. 133. See Fig. 133A.

Consider for a moment what will happen when the vessel has been filled with water, and the spindle is rotated. A bodily motion will be communicated to the water by the moving arms. Almost immediately, however, the water will be brought to rest after impinging against the fixed vanes. As in the previous experiment, the kinetic energy possessed by the moving water will thus be converted into heat.

The method used for setting the radial arms in motion, and measuring the work performed, is shown in Fig. 135. The spindle was attached to a drum *f*, round which two pieces of twine were wound side by side, in such a manner that both left it at the same level, but at the opposite extremities of a diameter, so that when equal forces were applied to the two pieces of twine the spindle was caused to rotate. The pieces of twine were wound round discs *a*, *a*, supported by means of axles mounted on friction wheels *dd*, *dd*.

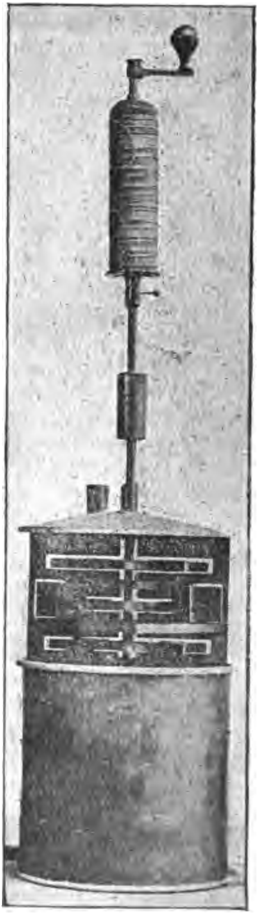

FIG. 134.—Joules's calorimeter, with the stationary vanes and the movable arms raised so as to be exposed to view. (From a photograph.)

Leaden weights *e*, *e*, were hung from strings wound round the rollers *p*, *p*, which were connected with the discs *a*, *a*.

Supposing the weights to have been raised to their highest level, and the temperature of the water in AB to have been noted, the subsequent procedure was as follows. The weights were released, and the paddles set in motion. The work done in any interval of time will be equal to the sum of the products of the forces acting on the weights *e*, *e*, into the respective distances through which they have fallen. When these weights had reached the ground, having fallen through known distances, the temperature of the water in the calorimeter was again noted. The drum *f* was then detached from the spindle by removing the pin *p*, and the weights were again raised to their highest level by turning the handle at the top of *f*. The pin *p* was then replaced, and the above procedure repeated.

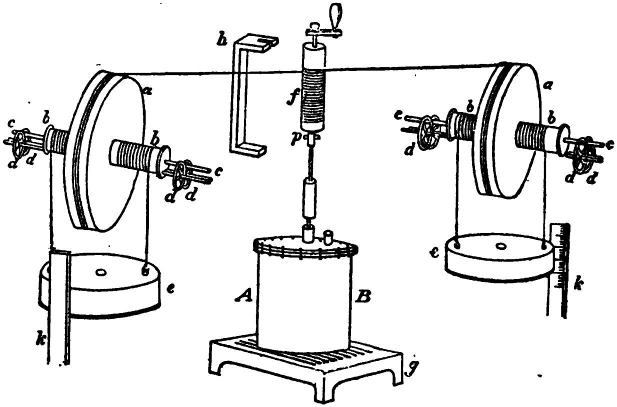

FIG. 135.—Joule's arrangement for determining the mechanical equivalent of heat. (The calorimeter AB, with the spindle, &c., are separately shown in Fig. 134.)

A mercury thermometer reading to $\frac{1}{300}$° C. was used to indicate the temperature of the water in the calorimeter.

In a particular experiment, the mass of both the weights *e*, *e*, was 26,320 grams, and each fell through a distance of 160·5 cms. twenty times in succession. The work performed was then equal to

$$20 \times 160{\cdot}5 \times 26{,}320 \times 981 = 8{\cdot}287 \times 10^{10} \text{ ergs.}$$

The water equivalent of the calorimeter AB and its contents was 6316 grams, and the rise in temperature during the experiment was ·3129° C.

Hence the heat produced =

$$6316 \times {\cdot}3129 = 1977 \text{ therms.}$$

$$\therefore J = \frac{\text{Work performed}}{\text{Heat produced}} = \frac{8{\cdot}287 \times 10^4}{1{\cdot}977 \times 10^3}$$

$$41{\cdot}9 \times 10^6 = \text{ergs per therm.}$$

Corrections.—Experiments were performed to determine the magnitude of the corrections for the following sources of error.

1. *Cooling of the calorimeter.*—The rate of change of the temperature of the calorimeter and its contents was determined immediately before the commencement, and again immediately after the conclusion, of an experiment. Thus the rate at which heat was gained or lost by radiation or convection could be determined. For method of applying this correction see p. 131.

2. *Velocity of weights on reaching the floor.*—The above calculation is made on the assumption that all of the work performed is used up in heating the water. If, on the other hand, the weights reach the floor whilst moving with an appreciable velocity, the kinetic energy which they possess the instant before they are brought to rest must be subtracted from the total work performed, in order to obtain the work utilised in heating the calorimeter. In Joule's experiments, the final velocity of the weights was about 6·16 cms. per second.

3. *Elasticity of the cords.*—The cords were initially stretched by the weights hung from them, so that they contracted after the weights had reached the ground, thus causing a further small rotation of the paddles, and a further evolution of heat.

4. *Friction of the pulleys.*—The force necessary to maintain

the weights moving uniformly, when impeded only by the friction of the pulleys, &c., was determined by disconnecting the drum *f* (Fig. 135), and arranging that the fall of one weight should necessitate the raising of the other. Small masses of metal were then added to one of the weights *e*, till a uniform velocity equal to that attained in the experiment was produced.

5. *Energy lost from vibrations.*—A humming sound was produced by the motion of the paddles, and the energy which was thus radiated in the form of sound waves was estimated.

Rowland's Experiments.—In 1879, Prof. H. A. Rowland, of Baltimore, U.S.A., published an account of a careful repetition of Joule's work. The weak points in Joule's determination of the mechanical equivalent were as follows :—

1. Joule's mercury thermometer was not compared with an air thermometer, so that the measurements of temperature were not quite certain (*see* Chap. II.).

2. The whole rise in temperature during a single experiment was small.

3. It was assumed by Joule, on the authority of Regnault, that the specific heat of water between 0° and 100° was constant (*see* Chap. VI., p. 134).

The method used by Rowland may be understood from an examination of Fig. 136. The calorimeter A was attached to a vertical shaft BC, which in its turn was fastened to a torsion wire CD. A horizontal arm attached to the shaft BC, carried weights w_1, w_2, which could be moved so as to vary the moment of inertia of the suspended parts. The shaft BC passed through the centre of a circular disc E, to which it was firmly attached. Silk cords which passed over the idle pulleys p_1, p_2, and were attached to weights W_1, W_2, were wound round the disc E in such a manner that they left it tangentially at the opposite extremities of a diameter, and exerted a couple tending to rotate the disc.

A steel axle passed upwards through the bottom of the calorimeter, and carried a set of paddles, each pierced by numerous holes. These paddles moved between fixed vanes attached to the calorimeter. The axle was rotated by the aid of the wheel *g*, which in its turn was driven by a steam engine.

When the paddles were rotated, it was found that the temperature of the calorimeter and the water which filled it could be increased at the rate of 45° C. per hour.

The method of measuring the work performed was somewhat different from that used by Joule in his earlier experiments

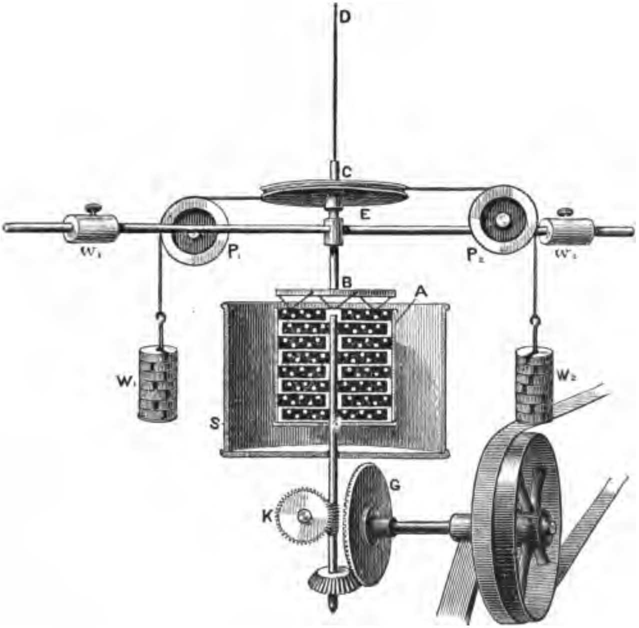

FIG. 136.—Rowland's arrangement for determining the mechanical equivalent of heat.

(p. 274), though agreeing substantially with the arrangement used in his 1878 determination.

The radial paddles set the water in movement, and in so doing were subjected to a pressure tending to oppose their motion. Let us assume that a force of f_1 dynes is exerted on an element of area of one of the paddles at a distance r_1 cms. from the axis of rotation. Thus the work done in overcoming this force during one second (the paddles having made n revolutions in that interval), is equal to

$$n \times f_1 \times 2\pi r_1 = 2\pi n r_1 f_1$$

Similarly, the work performed in overcoming the force f_2, on an element of area at a distance r_2, during the same interval, is equal to

$$2\pi n\, f_2 r_2.$$

Hence, the total work performed in one second is given by the expression

$$2\pi n \Sigma fr,$$

where Σfr denotes the sum of the products of the forces exerted on the various elements of all the paddles into the respective distances of their points of application from the axis of rotation.

The moving water, when brought to rest by the stationary vanes, exerts a force on these latter tending to rotate the whole calorimeter. If a force F_1 is exerted on an element of area of one of the stationary vanes, at a distance R_1 from the axis of suspension, then the resulting couple tending to rotate the calorimeter will be given by

$$F_1 R_1.$$

The total couple tending to rotate the calorimeter will be equal to

$$\Sigma FR,$$

the sum of the products of the forces exerted on the various elements of area of all the stationary vanes, into the respective distances of their points of application from the axis of suspension.

But in a similar manner it may be shown that

$$\Sigma fr$$

represents the couple opposing the motion of the paddles. Further, since action and reaction are equal in magnitude, we have

$$\Sigma fr = \Sigma FR.$$

Now when the paddles have been rotating for a short time, the calorimeter will have been rotated through a certain angle, and will then remain stationary. The couple resisting the rotation of the calorimeter comprises :—

1. That due to the tension of the silk cords wound round E. Let d be the diameter of the disc E, and w the mass attached to either silk cord. Then, since these cords leave the disc tangentially at opposite ends of a diameter, we have, denoting the acceleration due to gravity by g,

Couple due to the tension of the silk cords $= wgd$.

2. A further couple C will be exerted by the suspending wire. This must be determined by experiment.

Finally, we have

$$\text{Couple resisting rotation of calorimeter} = wgd + \mathrm{C}.$$

But since the calorimeter is supposed to be in a position of equilibrium, the couple resisting rotation must be equal to that tending to produce rotation.

$$\therefore \Sigma \mathrm{FR} = wgd + \mathrm{C}.$$

Hence, finally, the work performed during one second is equal to

$$2\pi n \Sigma fr = 2\pi n \Sigma \mathrm{FR} = 2\pi n(wgd + \mathrm{C}).$$

Those familiar with mechanics will recognise that the whole arrangement above described is in reality a particular form of absorption dynamometer.

It was found by Rowland that the amount of energy required to heat a given quantity of water through 1° C., has a minimum value at 29° C. By careful calorimetric experiments, Rowland satisfied himself that the specific heat of water has a minimum value, and this result has since been confirmed by other observers (see Chap. VI., p. 134.)

Rowland also compared the thermometer used by Joule with the air thermometer, and reduced Joule's results to metre-kilograms per calorie (see pp. 141 and 265) at the latitude of Baltimore. The mean values thus obtained were :—

Joule's value . .	426·75 at 14·6° C.
Rowland's mean value	427·52.

Hirn's Experiments.—Two interesting methods of determining the value of J, which have been employed with considerable success by Hirn, may here be mentioned.

1. If a piece of lead be beaten with a hammer, it will become heated. The kinetic energy possessed by the hammer at the instant before it strikes the lead is converted into heat when the lead is struck, and the hammer brought to rest. Nearly all of the heat produced in the lead is due to molecular friction during the deformation of the lead. Owing to the fact that lead is an inelastic substance, there is little tendency for the hammer to rebound. Further, only a very small amount of energy is lost in the production of sound.

The arrangement used by Hirn was designed to take advantage of the above properties of lead. A cylindrical mass of that metal was hollowed out so as to form a vessel with very thick walls. This was hung by means of ropes, as shown at P, Fig. 137, so that one end rested against an iron disc, B, attached to a massive prismatic block of sandstone. This block was suspended by four ropes, as shown in the figure, so that it could only move in a vertical plane, with its axis horizontal. A cylindrical mass of iron A was suspended in a similar manner, so that when at rest its end touched one extremity of the lead vessel.

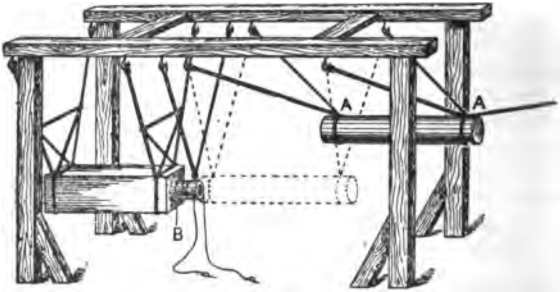

FIG. 137.—Hirn s arrangement for determining the mechanical equivalent of heat.

In order to make an experiment, the iron cylinder was pulled back into a position such as that shown in the figure. The difference between its height in this position and that when it hung freely was noted. The temperature of the lead was obtained by means of a sensitive thermometer. The iron bar was then set free, and on reaching its equilibrium position, it struck the lead. The height through which the sandstone block rose after impact, together with the height of recoil of the iron cylinder, were noted.

The lead vessel was then quickly removed, hung up by strings provided for that purpose, and partly filled with ice cold water. The temperature attained by the water after being stirred for some minutes was noted.

Let M_1 = mass of iron cylinder, in grams.
M_2 = mass of sandstone block, together with that of the iron attached to its end.
m_1 = mass of lead vessel.
s = specific heat of lead.
m_2 = mass of water at 0° C., poured into the leaden vessel.
H = height, in cms., through which the axis of the iron cylinder was initially raised.
h_1 = height of recoil of iron cylinder.
h_2 = height through which the sandstone block rose after impact.
t_1 = initial temperature of lead.
t_2 = final temperature of lead and water.

The kinetic energy gained by M_1 grams in falling through H cms. $= M_1gH$.

Energy converted into the potential form during the rise of the sandstone block, and the recoil of the iron cylinder $= M_1gh_1 + M_2gh_2$.

$\therefore$ Energy converted into heat $= g\,(M_1(H - h_1) - M_2h_2)$.

Heat produced $= m_1s\,(t_2 - t_1) + m_2t_2$.

$$\therefore\ J = \frac{g\{M(H - h_1) - M_2h_2\}}{m_1s\,(t_2 - t_1) + m_2t_2}.$$

The following figures refer to a particular experiment.

M_1 = 350,000 grams.
M_2 = 941,000 ,,
m_1 = 2,948 ,,
m_2 = 18·5 ,,
s = 0·314 ,,

H = 116·6 cm.
h_1 = 8·7 cm.
h_2 = 10·3 cm.
t_1 = 7·873° C.
t_2 = 12·1° C.

Substituting these values in the above formula, and taking 981 as the value of g, we get

$$J = \frac{981\{350{,}000(116{\cdot}6 - 8{\cdot}7) - 941{,}000 \times 10{\cdot}3\}}{2948 \times {\cdot}0314 \times 4{\cdot}227 + 18{\cdot}5 \times 12{\cdot}1}$$

$$= \frac{981 \times 28{,}070{,}000}{391{\cdot}3 + 223{\cdot}8} = \frac{27{,}540{,}000{,}000}{615{\cdot}1} = 44{\cdot}7 \times 10^6 \text{ ergs per therm.}$$

Values more nearly equal to 42×10^6 ergs, the accepted value for J, were obtained in some of Hirn's experiments.

2. Another method used by Hirn was to measure the amount of steam, at an observed temperature and pressure, which entered the cylinder of a steam engine in a given time, and to

determine the heat remaining in the waste steam by passing it through cold water, of which the initial and final temperatures were noted. Thus the heat which entered the cylinder could be calculated, and on subtracting the waste heat from this value, the amount of heat utilised in driving the engine could be determined. The work performed was determined by the aid of an indicator diagram. Thus the value of the ratio

$$\frac{\text{Work performed}}{\text{Heat which disappeared}} = J$$

was calculated. The value thus obtained differed little from that found by Joule.

It may be noted that in the experiments previously described, energy was converted into heat, whilst in this last experiment, the converse process of converting heat into work was used.

The First Law of Thermodynamics.—This is a generalisation of the results of the foregoing experiments. According to Maxwell, it may be expressed as follows:— **When work is transformed into heat, or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.**

From a comparison of the results of Rowland, and of Reynolds and Moorby, together with the results of the investigation on the specific heat of water from 0°C. to 100°C., mentioned on p. 135, Prof. Callendar gives $41{\cdot}80 \times 10^6$ as the most probable value of the Mechanical Equivalent of Heat; the unit of heat adopted being that required to raise 1 gram of water through 1°C., at 20° C.

SUMMARY.

Caloric.—In the earlier theories, heat was considered to be an elastic fluid which was absorbed by bodies during a rise of temperature, and given up by bodies during a fall of temperature.

Rumford showed that an inexhaustible supply of heat could apparently be obtained by rubbing one body against another. This was inconsistent with the assumption that heat was a fluid.

Davy showed, by rubbing two pieces of ice together, that an unlimited supply of heat could thus be obtained.

Energy and heat.—When a moving body is brought to rest under such conditions that its kinetic energy has no opportunity of being transformed into potential energy, heat is produced.

Joule showed that when a moving body is brought to rest the energy which disappears, is equivalent to the heat produced. Water was first set in motion and then immediately reduced to rest, and the quantity of heat generated was measured. He thus found that 42 *million ergs of energy is equivalent to* 1 *therm or gram-calorie.* In other words, the heat produced when 42 million ergs of energy disappears would raise the temperature of one gram of water through one degree Centigrade.

Rowland has repeated Joule's work, using mercury thermometers which had been compared with a standard air thermometer. His arrangement permitted of a rapid rise of temperature, and his results showed that the specific heat of water varied with the temperature.

Hirn determined the mechanical equivalent of heat by allowing a mass of iron, moving with a considerable velocity, to strike on a mass of lead. The heat produced in the lead was measured, and results agreeing with Joule's were obtained. He also measured the temperature and pressure of the steam entering the cylinder of a steam engine, and conducted the waste steam through a calorimeter. Thus the heat entering the cylinder, as well as that leaving it, was determined. The heat which disappeared was found to be equivalent to the work performed by the engine.

The First Law of Thermodynamics.—*When work is transformed into heat, or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.*

QUESTIONS ON CHAPTER XII.

(1) Determine, having given the following data, from what height a lead bullet must be dropped, in order that it may be completely melted by the heat generated by the impact, assuming that four-fifths of the heat generated remains in the bullet.

Heat required to raise 1 gram of lead from the initial temperature of the bullet to the melting point, and to melt it, 15 units; mechanical equivalent of heat 42×10^6 ergs. Value of g, 980 cm. per sec. per sec.

(2) A cannon ball, the mass of which is 100 kilograms, is projected with a velocity of 500 metres per second. Find in C.G.S. units the amount of heat which would be produced if the ball were suddenly stopped.

(3) If an engine working at 622·4 horse-power keeps a train at constant speed on the level for 5 minutes, how much heat is produced, assuming that all the missing energy is converted into heat?

Take the mechanical equivalent = 778 [ft.-lbs. per lb. of water per degree F.]; one horse-power = 33,000 ft.-lbs. per minute.

(4) Describe the method of determining the value of J which you consider the best. Give full reasons for your answer, pointing out the merits and defects of the method you adopt.

(5) With what velocity must a lead bullet at 50° C. strike against an obstacle in order that the heat produced by the arrest of its motion, if all produced within the bullet, might be just sufficient to melt it?

Take specific heat of lead $=0{\cdot}031$.
,, melting point $=335°$ C.
,, latent heat of fusion $=5{\cdot}37$.

(6) What do you understand by the Mechanical Equivalent of Heat? Taking the mechanical equivalent as 1,400 ft.-lbs. per degree Centigrade per lb. of water; determine the heat produced in stopping by friction a fly-wheel 112 lbs. in mass, and 2 feet in radius, rotating at the rate of one turn per second, assuming the whole mass concentrated in the rim.

(7) Give an outline of the arguments which lead to the conclusion that heat is a mode of motion.

(8) What is meant by saying that heat is a form of energy? How has the amount of energy corresponding to a unit of heat been determined?

(9) Write a short account of the methods which have been employed to determine the Mechanical Equivalent of Heat, giving an account of the corrections required in each method and the relative advantages of the various methods.

(10) What is meant by the statement that the Mechanical Equivalent of Heat is 427 metre grams per gram calorie?

(11) Define the Mechanical Equivalent of Heat.

If the kinetic energy contained in an iron ball, having fallen from rest through 21 metres, is sufficient to raise its temperature through 0·5° C., calculate a value for the Mechanical Equivalent of Heat. Assume $g = 980$ cm. per sec. per sec., and specific heat of iron 0·1.

(12) Briefly describe one of the ways in which the amount of energy equivalent to a given amount of heat has been determined. Explain what is meant by expressing the specific heat of water in ergs per gram, and state its value either in these units or in gravitation ft.-lbs. per lb.

CHAPTER XIII

THE KINETIC THEORY OF GASES

Heat and Energy.—As a result of experiments, some of the most important of which have been described in the last chapter, it has been conclusively established that there is an exact equivalence between heat and energy ; in other words, if a moving body is suddenly brought to rest under such conditions that its kinetic energy has no opportunity of passing into the potential form, then a quantity of heat will be generated proportional to the kinetic energy possessed by the body at the instant before its motion was arrested.

The object of the present chapter is to present, in a simple form, some of the most important points of a theory, which has been found capable of explaining most of the physical properties ot gases in terms of the motions of their ultimate constituent particles.

Consider for a moment what happens when a drop of mercury falls from a height on to a plate of glass. The mercury moves *as a whole* through the air ; *i.e.*, there is practically no relative motion between its parts up to the instant when the glass is struck. Just before striking the glass, the mercury possesses a certain amount of kinetic energy, equal to

$$\frac{1}{2} mv^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(p. 263)}$$

where m is its mass, and v its velocity. On reaching the glass. the motion of the drop of mercury *as a whole* ceases ; relative motions between different parts of the mercury takes its place. Thus, it becomes divided into numerous droplets, which splash off in different directions with various velocities. The sum of the kinetic energies possessed by these various droplets will, however, be equal to the kinetic energy possessed by the main drop at the instant before it struck the glass.

The nature of the process here illustrated may be said to consist in the production of relative motion in the several parts of a body, as a result of the arrest of the motion of the body as a whole.

We have already seen that various philosophers, from Sir Francis Bacon to Count Rumford, felt assured that there was a more or less definite relation between heat and motion. We will here provisionally assume that the heat generated in a body when its motion is suddenly arrested, is associated with the production of relative motions of the constituent molecules.

Molecules and Atoms.—Chemical experiments have led to the conclusion that matter is not infinitely divisible, but that if a substance be continually divided and subdivided, a stage will at last be reached when the products of further division will possess properties different from those of the substance divided. Thus, if a drop of water were continually divided and subdivided, a stage would at length be reached where further division would produce two gases—oxygen and hydrogen.

A molecule is the smallest portion of a substance which can exist, while still possessing the distinctive properties of that substance.

An atom is the smallest portion of a substance capable of an independent existence. An atom is therefore indivisible.

A substance may consist of molecules, each of which comprises only a single atom (*e.g.*, mercury vapour, argon, helium, krypton, &c., which are called monatomic substances); or, the constituent molecules may comprise two or more atoms. Thus, hydrogen and oxygen consist of molecules, each of which comprises two atoms; carbon dioxide and sulphur dioxide gases consist of molecules, each comprising three atoms; whilst the vapour of alcohol consists of molecules, each of which comprises nine atoms.

We will assume that the essential difference between a body when hot and when cold lies in the fact that in the former condition the *molecules* are in a more violent state of agitation than in the latter.

Molecular Conditions of Solids, Liquids, and Gases.—*Gases.*—A few minutes after the stopper has been removed from a bottle containing ammonia, the pungent odour of the vapour of that substance can be perceived throughout the room. This proves that, in the case of gases, a molecule is capable of moving with comparative freedom from one position to another.

Liquids.—Experiments with liquids show, that though we must consider their constituent molecules to be capable of moving continuously from place to place, yet the rate at which such transfer takes place is small when compared with the rate of transfer in gases.

Solids.—In solids we must consider that the molecules are incapable of moving continuously from place to place, and that the motions which are associated with heat take place about fixed positions. Sir William Roberts-Austen has indeed shown that if a sheet of gold be laid on the plane surface of a block of lead, the gold will gradually diffuse into the lead. But the rate at which this diffusion takes place is very slow, so that the molecular condition of a solid may be assumed to be substantially that above described.

In order to account for the phenomena connected with capillarity and surface tension, it is necessary to assume that the molecules of a liquid are so close together that the effects of their mutual attractions must be taken into account. In solids this mutual attraction must in some way or another give rise to cohesion. Finally, we may consider a gas to consist of molecules in rapid motion, the progress of a molecule in any direction being limited simply by the occurrence of collisions with other molecules. The average distance between neighbouring molecules is supposed to be so great that the effects of their mutual attractions may be left out of account.

To gain greater definiteness in our ideas, let us consider what would happen if a perfectly elastic sphere were set in motion within an enclosure bounded by perfectly rigid walls. Every time that the sphere impinged on one of the walls, the component of its velocity perpendicular to the wall would be reversed, and a certain force would be exerted on the wall. No work would be performed, and the sphere would afterwards be moving with the same velocity as previously. Thus the kinetic energy of the sphere would remain constant.

Let us now assume that a number of perfectly elastic spheres are inclosed by a vessel with rigid walls. The *magnitude* of the velocity of a sphere will not be altered by impact at a wall, but when two of the spheres meet, their velocities before and after impact will not necessarily be equal. Thus the energy possessed by a particular sphere will vary from time to time. On the other hand, the total energy possessed by all the spheres will remain constant, since no energy is communicated to the walls, and the energy lost at any particular impact by one sphere is necessarily gained by another.

If an inclosure such as we have been considering were set in motion and then brought to rest, the result would be that the relative velocities of the contained spheres would be augmented, and thus the total kinetic energy possessed by them would be increased. On the supposition that the heat contained by a body is really only another name for the kinetic energy associated with the linear motions of its constituent molecules, this case would illustrate the rise in temperature of a body when its motion is suddenly arrested (*see* Chap. XII).

Pressure Exerted by a Gas.—If we consider a gas to consist of elastic spheres in rapid motion, continually colliding with each other, or rebounding from the walls of the containing vessel, it is clear that every time the momentum of a molecule is reversed by impact with a wall of the vessel, a certain force will be exerted on the latter. Let us suppose, for instance, that the gas is contained in a cylinder, one end of which is closed permanently, whilst a frictionless piston prevents the escape of the gas from the other end. Then the reversal of the momentum which occurs when a molecule strikes the piston, will tend to move the piston outwards, so as to increase the volume occupied by the gas. It remains to be shown whether the force thus exerted by the successive impacts of the various molecules on the piston would produce a pressure varying inversely as the volume occupied by the molecules.

To deduce Boyle's Law from the Kinetic Theory of Gases.

Let us assume—

(1) That the diameter of a molecule is very small in comparison with the distance traversed between successive encounters.

(2) That a very large number of molecules exist even in the smallest volume of gas with which we are acquainted.

(3) That the molecules are moving with considerable velocities, so

that a large number of encounters occur in an exceedingly short interval of time.

(4) That the time occupied by an encounter of two molecules is very small in comparison with the interval elapsing between successive encounters.

(5) That the molecules are on an average so far separated one from another that the effects of their mutual attractions or repulsions may be neglected.

Let us suppose, at the outset, that a certain quantity of gas is contained in a cubical vessel, each edge of which is 1 cm. long. Then the *force produced by the reversal of the momenta* (p. 262) *of the molecules impinging on one face of the cube will be equal to the pressure (force per unit area) exerted by the gas.*

$P = \frac{F}{a}$

$'' = \frac{MV}{t}$

Let there be *n* molecules contained in the vessel, *i.e.*, in one cubic centimetre. Then, on an average, each molecule occupies a small cube the volume of which is $\frac{1}{n}$ c.c. The molecules move across these elementary cubes, the directions of their motions being reversed by impact on the walls of the containing vessel, when one of these forms a bounding surface of an elementary cube. When a molecule moves out of an elementary cube, another will, on an average, immediately enter and take its place, so that the net result is the same as if each molecule travelled to and fro across the elementary cube which it occupies, and rebounded whenever it reached one of the faces of the elementary cube.

A molecule will move freely, in the interval between successive rebounds. The distance so traversed will obviously be equal to the length of an edge of the elementary cube in which the molecule moves backwards and forwards; it is termed the *mean intermolecular distance* of the molecules.

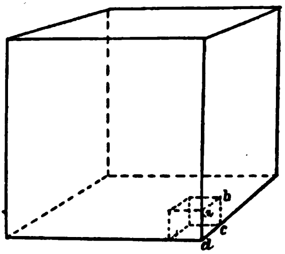

FIG. 138.—Cubical vessel enclosing gas molecules.

Let *abcd* (Fig. 138), represent a face of one of the *n* elementary cubes occupied by the gas molecules, this face being in the plane of one of the bounding surfaces of the cubical containing vessel. Then, if we consider that the contained molecule moves backwards and forwards along the normal to *abcd*, with an average velocity of V cms. per second, it can easily be seen that it will traverse a distance 2δ *between successive impacts on abcd*, δ being the length of an edge of the elementary cube, or the mean intermolecular distance of the gas molecules.

But the volume of the elementary cube $= \delta^3 = \frac{1}{n}$ c.c.

$$\therefore\ \delta = \left(\frac{1}{n}\right)^{\frac{1}{3}} \text{cm.}$$

The number of impacts per second on *abcd* = distance traversed in one second ÷ distance traversed between succeeding impacts on *abcd*

$$= \frac{V}{2\delta} = \frac{n^{\frac{1}{3}}}{2}V.$$

If m = the mass of a molecule, then the momentum of a molecule just before impact $= mV$ (p. 262), and just after impact $= -mV$, since during impact the velocity is changed from $+V$ (toward the surface *abcd*) to $-V$ (in the opposite direction). Hence change of momentum at a single impact $= 2mV$, and this change takes place $\frac{n^{\frac{1}{3}}}{2}V$ times in each second.

Therefore a change of momentum per second equal to

$$\frac{n^{\frac{1}{3}}}{2}V \times 2mV = n^{\frac{1}{3}}mV^2$$

takes place at the surface *abcd*. But change of momentum per second = force (p. 262). Therefore a force of $n^{\frac{1}{3}}mV^2$ dynes is exerted on the area *abcd*.

To find the force exerted on the face of the centimetre cube, notice that

$$\text{Area } abcd = \delta^2 = \left(\frac{1}{n}\right)^{\frac{1}{3}} \times \left(\frac{1}{n}\right)^{\frac{1}{3}} \text{ sq. cm.} = \frac{1}{n^{\frac{2}{3}}} \text{ sq. cm.}$$

$$\therefore \text{ Number of squares such as } abcd \text{ in 1 sq. cm.} = \frac{1}{\frac{1}{n^{\frac{2}{3}}}} = n^{\frac{2}{3}}.$$

$\therefore$ *Total force on a face of the centimetre cube* = pressure of the contained gas $= n^{\frac{2}{3}} \times n^{\frac{1}{3}}mV^2 = nmV^2$ dynes. Taking account of the fact that a molecule may not always be moving with the same velocity, and that the velocities of different molecules at the same instant are not exactly equal, we must let V^2 represent the mean value of the square of the molecular velocity.

Mean Square Velocity.—Let us suppose that equal numbers of molecules are moving at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 cms. per second respectively. Then the *mean square velocity* =

$$\frac{1^2+2^2+3^2+4^2+5^2+6^2+7^2+8^2+9^2+10^2}{10} = 38{\cdot}5.$$

The square root of the mean square velocity = $\sqrt{38{\cdot}5} = 6{\cdot}2$.

The mean velocity of the molecules =

$$\frac{1+2+3+4+5+6+7+8+9+10}{10} = 5{\cdot}5.$$

Hence, we see that the mean molecular velocity is not exactly equal to the square root of the mean square of the molecular velocities. The difference between these numbers will not, as a general rule, be as great as that just obtained, since the simultaneous variations of molecular velocities will generally be less than that assumed above. Hence, we shall commit no great error in taking V (which is really the square root of the mean square velocity) as equal to the mean molecular velocity.

We have, up to the present, supposed that all of the molecules are moving either backwards or forwards along a line perpendicular to *abcd*. As a matter of fact, if any three lines are drawn at right angles to each other (*e.g.*, parallel to the adjoining edges of the centimetre cube), as many molecules will, at any instant, be moving along one of these lines as along another. Thus, since only one third of the total number of molecules should be assumed to be moving in any one direction at any instant, we must write $\frac{n}{3}$ instead of n in the equation just obtained. We thus obtain the result that

Pressure on one face of the centimetre cube $= p = \frac{n}{3}m\text{V}^2$ dynes.

Multiplying both sides of the equation by v, which may represent any volume measured in c.cs., we get

$$pv = \frac{nm}{3}v\text{V}^2.$$

Now nm = the mass of n molecules, originally occupying 1 c.c. ∴ nm = density of the gas at the initial pressure, and a temperature which has been assumed throughout the above calculation to be constant.

∴ nmv = mass of gas which occupies, at the temperature in question, a volume v under a pressure $= \frac{nm}{3}\text{V}^2$. Let this mass be denoted by M. Then

$$pv = \frac{\text{M}}{3}\text{V}^2.$$

Consequently the relation pv = constant will hold as long as V^2, the average value of the square of the velocities of the molecules of the gas, remains unaltered.

But since $\frac{1}{2}mV^2$ = the kinetic energy of a gas molecule due to its linear motion, $\frac{1}{2}MV^2$ = the kinetic energy possessed by a mass M of the gas, in virtue of the linear motions of its constituent molecules. Hence, since we have assumed that an increase in the kinetic energy of the molecules of a gas is the cause of a rise in its temperature, we see that the relation

$$pv = \text{constant}$$

will hold as long as the temperature remains unaltered.

Relation between the Temperature of a Gas and the Linear Velocities of its Constituent Molecules.—In accordance with the method of measuring temperature by the aid of a gas thermometer (*see* Chap. V.), we have the relation

$$pv = RT$$

where T is the absolute temperature of the gas. Compare this equation with the expression

$$pv = \frac{M}{3}V^2$$

M represents the mass of the gas, which of course remains constant. We therefore see that

$$T \propto V^2.$$

i.e., the absolute temperature of a gas is proportional to the mean square of the molecular velocity, or to the kinetic energy possessed by the molecules of the gas, in virtue of their linear velocities.

Absolute Zero.—It can easily be seen that if we take a volume v of gas, and cool it under constant pressure, we shall have $v = o$ when $V^2 = o$.

In the same manner it can be shown that if a gas is cooled at constant volume, the pressure exerted by the gas will become equal to zero when $V^2 = o$, and therefore $T = o$.

Hence the absolute zero of temperature will be reached when the linear velocities of the molecules have been reduced to zero *i.e.*, when the molecules have een brought to rest.

Avogadro's Law.—From the above it becomes evident that the temperature of a gas molecule is proportional to the kinetic energy possessed by it in virtue of its linear velocity.

It is generally assumed that, at a given temperature, the average kinetic energies possessed by single molecules of different gases have equal values. Thus with a gas A, of which a molecule possesses a mass m_1 and an average velocity V_1, at absolute temperature T, we have

Kinetic energy of molecule of gas A at temperature $T = \frac{1}{2}m_1V_1^2$.

If m_2 and V_2 have similar meanings with regard to a molecule of a gas B at the same absolute temperature T, we have

Kinetic energy of molecule of gas B at temperature $T = \frac{1}{2}m_2V_2^2$.

According to the above assumption, we have

$$\frac{1}{2}m_1V_1^2 = \frac{1}{2}m_2V_2^2$$

$$\therefore\ m_1V_1^2 = m_2V_2^2 \quad \ldots \ldots \quad (1)$$

Let us suppose that two centimetre cubes are respectively filled with the gases A and B, at the same temperature T and pressure p. Then, if n_1 and n_2 are the numbers of molecules in the respective cubes, we have

$$\therefore\ p = \frac{1}{3}n_1m_1V_1^2 = \frac{1}{3}n_2m_2V_2^2 \quad \text{(p. 293).}$$

$$\therefore\ n_1m_1V_1^2 = n_2m_2V_2^2 \quad \ldots \ldots \quad (2)$$

Dividing by (1), we get

$$n_1 = n_2 \quad \ldots \ldots \quad (3)$$

This result, expressed in words, states that at the same temperature and pressure, equal volumes of all perfect gases comprise the same number of molecules. This is the celebrated generalisation known as *Avogadro's Law.*

It should be remembered that this law is only strictly true for substances possessing the properties of perfect gases.

Graham's Law of Diffusion.—From (2) above, we have the relation

$$\frac{V_1}{V_2} = \sqrt{\frac{n_2m_2}{n_1m_1}} = \sqrt{\frac{\text{density of B}}{\text{density of A}}}$$

In words, we may state that the average velocities (*see* p. 293) of the molecules of different gases at a given temperature are inversely proportional to the square roots of the densities of the respective gases.

Graham found that gases diffused through porous plugs at rates inversely proportional to the square roots of the respective densities of the gases.

Problem.—Determine the mean linear velocity of hydrogen molecules at a temperature of 0° C.

Let M be the mass of hydrogen which occupies a litre (1,000 c.cs.) at 0° C. and 760 mm. pressure. Thus, from the relation

$$pv = \frac{M}{3}V^2$$

remembering that p must be expressed in dynes, we get

$$(76{\cdot}0 \times 13{\cdot}6 \times 981) \times 1{,}000 = \frac{M}{3}V^2. \quad \therefore V^2 = \frac{3 \times 76 \times 13{\cdot}6 \times 981 \times 1{,}000}{M}.$$

But M = ·0896 grams.

$$\therefore V = \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 981 \times 1{,}000}{{\cdot}0896}} = \sqrt{\frac{3{\cdot}042 \times 10^9}{{\cdot}0896}}$$

$$= 1{\cdot}84 \times 10^5 \text{ cms. per second.}$$

Atomic Heats.—If equal increments of energy are necessary in order to raise the temperatures of single molecules of different substances through a given range, Dulong and Petit's Law, that equal numbers of atoms of different elementary substances require equal quantities of heat in order to raise their temperatures by 1°C., follows as a matter of course.

Pressure of a Mixture of Gases or Vapours.—Dalton's Law (p. 230), states that the pressure of a mixture of gases and vapours enclosed in a given space is equal to the sum of the pressures which the gases, &c., would severally exert when individually occupying the given space at the same temperature. This follows directly from the kinetic theory of gases. For the pressure p exerted by a mixture of two gases, of which the molecules possess masses m_1 and m_2, and velocities V_1 and V_2, is given by

$$p = \tfrac{1}{3}n_1m_1V_1^2 + \tfrac{1}{3}n_2m_2V_2^2$$

the numbers of molecules of different kinds in 1 cc. being n_1 and n_2 respectively. This expression is equal to the sum of the pressures $\frac{1}{3}n_1m_1V_1^2$ and $\frac{1}{3}n_2m_2V_2^2$, which would be exerted by n_1 molecules of the first gas, and n_2 molecules of the second, if these were severally enclosed in separate vessels, each of unit volume.

Work Performed in Compressing a Gas Isothermally.—Let ADBC represent a cylinder, the space between the closed end AC and the air-tight piston EF being filled with a gas. (Fig. 139.)

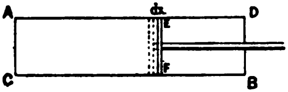

FIG. 139.—Cylinder and piston for compressing a gas.

Let the pressure, when the piston is at EF, be equal to p, the volume of the enclosed gas being v. Then, since pressure = force per unit area, the total force with which the enclosed gas will resist a small inward motion of the piston $= p \times$ area of piston $= pa$, if $a =$ area of piston.

If the piston is moved inwards through a short distance dx, the work done will be equal to the product of the force opposing the motion of the piston (pa), into the distance (dx), through which the piston is moved. Let us call this element of work dW. Then

$$d\text{W} = pa \times dx = padx.$$

But $adx =$ the amount by which the volume of the enclosed gas has been decreased $= dv$ (say),

$$\therefore d\text{W} = pdv.$$

Let the curve AB (Fig. 140) represent the isothermal relation between the pressure and volume of the gas enclosed in the cylinder. Thus OD, Fig. 140, represents the volume v occupied by the gas when the piston is at EF, Fig. 139, and DC, Fig. 140, represents the pressure p to which it is subjected.

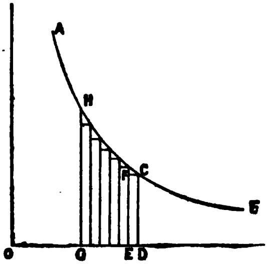

FIG. 140.—Graphic determination of work performed in compressing a gas.

Let DE $= dv$, the amount by which the volume of the contained gas is diminished when the piston is moved inwards through the distance dx. Then work done during the compression of the gas $= pdv =$ CD × ED = the area of the rectangle CDEF.

If the gas is further compressed, so that its volume is diminished by successive small decrements, from OD to OG (Fig. 140), it will be seen that the work done is equal to the sum of the areas of a number of rectangular strips, such as CDEF. Further, it is at once seen that the sum of the areas of these strips is approximately equal to the area enclosed by the curve HC, the two ordinates DC and GH, and the axis of volumes GD.

Now the kinetic energy possessed by the gas molecules at any time throughout the compression, is equal to

$$\frac{1}{2}MV^2$$

where M is the mass of the gas experimented upon, and V^2 is the mean square molecular velocity. V^2 must remain constant throughout the compression, since, by the terms of the inquiry, the temperature is maintained constant. Consequently the kinetic energy of the gas molecules remains constant.

The question now arises, what has become of the energy consumed in compressing the gas? The answer is, that heat has been developed as the gas was compressed, and has been given off to surrounding bodies as quickly as it was generated.

During the compression of the gas, the molecules which struck against the piston (which was moving inwards), rebounded with increased velocity. This accounts for the temporary heating of the gas. The extra energy so acquired was immediately transferred to the molecules composing the walls of the containing vessel, and was from these transferred to surrounding bodies.

Conversely, if the gas is allowed to expand isothermally from the volume represented by OG to that represented by OD, external work may be performed. The maximum value of this external work is equal to the area HCDG. At the same time the heat equivalent of the work performed is absorbed by the gas from surrounding bodies.

Internal Work of Expanding Gases.—We have hitherto assumed that the effects of any mutual attractions or repulsions exerted between neighbouring molecules of a gas may be neglected. An examination as to whether this assumption is permissible or not was made by Joule.

Joule's Experiments.—We have seen that when a gas expands, performing external work, a fall in its temperature will result, unless heat is communicated to it from surrounding bodies. Joule set himself to determine whether any temperature change occurs when a gas expands without performing external work. It is plain that this would happen if the mutual attractions or repulsions of molecules produced any appreciable effect. For if attractions are exerted between neighbouring molecules, work must be performed in separating them more widely, and this will entail a disappearance of a certain amount of heat, or molecular kinetic energy.

Two metal vessels, A, B, Fig. 141, were connected by means of a tube having a stop-cock at C. A was filled with dry air under a pressure of about twenty atmospheres, and B was exhausted. Both were then placed in a vessel filled with water so as to serve as a calorimeter.

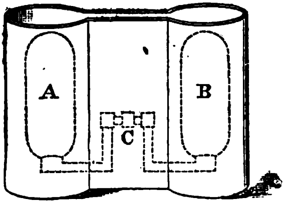

FIG. 141.—Apparatus used by Joule to determine the internal work performed during the free expansion of a gas. (P.)

The water was well stirred, and its temperature noted by the aid of a thermometer reading to $\frac{1}{200}$ of a Fahrenheit degree. The stop-cock C was then opened, and air allowed to flow from A to B until equilibrium was established. The temperature of the water was again observed. It was found to be equal to the initial temperature.

Now the only difference between the states of the gas at the beginning and end of the experiment was, that the molecules were further separated in one case than in the other. No external work had been performed, and any kinetic energy of motion as a whole, communicated at any time to a portion of the gas, must have been subsequently reconverted into heat by friction, as the gas was once more brought to rest. Since the temperature of the gas remained unaltered, no appreciable amount of heat could have been absorbed in performing internal work.

Joule also performed another series of experiments, in which the vessels A and B were inverted, and placed in separate calorimeters, a small calorimeter being also placed around the tap C.

It was found that the gas in the cylinder where the expansion occurred was cooled, whilst heat was generated in the cylinder into which the gas flowed, and at the stop-cock C. The total heat produced in B and at C was found to be exactly equal to that which disappeared from A.

Joule therefore concluded that *no internal work is performed when a gas expands*, or, in other words, that *the molecules of a gas are so far removed from each other that the effects of their mutual attractions or repulsions may be neglected.*

It may be remarked that the above experiment was not a very delicate one, since the thermal capacity of the calorimeter and water was many times greater than that of the gas. The results obtained may be taken as proving that no very considerable heating or cooling effect is associated with the expansion of a gas when no external work is performed. The later and more accurate experiments of Joule and Kelvin will be explained subsequently. (*See* Chap. XVIII.)

Relation between the Specific Heats of a Gas.— When heat is communicated to a quantity of gas the volume of which is kept constant, it may be utilised in the following ways :—

(1) In increasing the kinetic energy $\frac{1}{2}MV^2$ due to the linear velocity V of the molecules, M being the mass of the gas. This will correspond to a rise in temperature of the gas.

(2) The atoms within a molecule may be set in more violent relative motions. We may expect that the greatest quantities of energy will be absorbed in this manner by gases, the molecules of which comprise a large number of atoms.

(3) Different parts of the same atom may be set in relative motions. There is little doubt that this actually occurs ; but from the nature of the case we may consider the amount of energy used in this manner to be comparatively small.

When a gas is heated at *constant pressure*, additional energy to that specified above is required to perform external work. If the volume v of 1 gram of the gas is increased by dv, the pressure remaining at a constant value p, then the external work performed is equal to pdv. This will be equivalent to $\frac{pdv}{J}$ therms of heat.

Finally, let σ_p the specific heat of the gas at constant pressure,

σ_v = the specific heat of the gas at constant volume.

When the gram of gas is heated, at constant pressure, through a small range of temperature, dT, the heat communicated to it must be equal to

$$\sigma_p dT = \sigma_v dT + \frac{pdv}{J}.$$

If the gas obeys Boyle's Law, then pdv can at once be calculated. For we have

$$pv = RT$$
$$p(v + dv) = R(T + dT)$$
$$\therefore pdv = RdT.$$

Hence

$$\sigma_p dT = \sigma_v dT + \frac{RdT}{J}$$

$$\therefore \sigma_p = \sigma_v + \frac{R}{J}.$$

If σ_p, σ_v, and R are known, J can be calculated from this equation.

Example.—Having given, that 1 litre of hydrogen at 0° C. and a pressure of 760 mm. of mercury weighs ·0896 grams, and that $\sigma_p = 3\cdot409$, $\sigma_v = 2\cdot411$, calculate the value of J, the mechanical equivalent of heat.

We must first determine the value of R in the equation

$$\sigma_p = \sigma_v + \frac{R}{J}.$$

Now 1 gram of hydrogen will occupy a volume of

$$\frac{1,000}{\cdot0896} = 11,160 \text{ c.cs.}$$

Then, from the relation

$$pv = RT$$

we have, for a temperature of 0° C. ($T = 273$), expressing p in dynes,

$$76 \times 13\cdot6 \times 981 \times 11,160 = R \times 273$$

$$\therefore R = 4\cdot14 \times 10^7.$$

$$\therefore J = \frac{R}{\sigma_p - \sigma_v} = \frac{4\cdot14 \times 10^7}{3\cdot409 - 2\cdot411} = 4\cdot15 \times 10^7 \text{ ergs per therm.}$$

It was in this manner that Mayer determined the mechanical equivalent of heat. It must be remembered, however, that this method virtually assumes that no appreciable amount of internal work is performed when the volume of a gas is altered. The proof that this assumption was admissible was due to Joule.

Ratio of the specific heats of a Gas. (γ)

Let V^2 be the mean square of the molecular velocity of a gas at a particular temperature T (measured from the absolute zero). Then the kinetic energy possessed by 1 gram of the gas will be equal to

$$\tfrac{1}{2} \times 1 \times V^2 = \frac{V^2}{2} \text{ (p. 294).}$$

Further, since $M = 1$, we have

$$pv = RT = \tfrac{1}{3}V^2 \text{ (*see* p. 293).}$$

$$\therefore \tfrac{1}{2}V^2 = \tfrac{3}{2}RT.$$

Hence the increase, E, per degree centigrade, in the energy due to the linear velocities of the molecules in a gram of gas, is given by

$$E = \tfrac{3}{2}R.$$

Let e be the increase of energy per degree centigrade due to the relative motions of the atoms within the molecules comprised in the gram of the gas. Then, neglecting the mutual attractions or repulsions exerted by neighbouring molecules, we have

$$\gamma = \frac{\sigma_p}{\sigma_v} = \frac{E + e + p\,dv}{E + e} = \frac{\frac{3}{2}R + e + R}{\frac{3}{2}R + e} = \frac{5R + 2e}{3R + 2e}.$$

If $e = 0$, as we may assume to be the case in a monatomic gas, we have

$$\gamma = \tfrac{5}{3} = 1{\cdot}666.$$

For gases, each molecule of which comprises more than one atom, e will have a finite value. Also, the greater e is, the more nearly will the value of γ approximate to unity.

The following table gives the values of σ_p and σ_v, together with their ratio γ, for a number of gases and vapours.

Gas	Chemical Formula.	Number of Atoms in Molecule.	σ_p.	σ_v.	$\gamma = \frac{\sigma_p}{\sigma_v}$
Argon . . .	—	1	—	—	1·666
Oxygen . . .	O_2	2	0·2175	0·1551	1·40
Hydrogen . .	H_2	2	3·409	2·411	1·42
Chlorine . .	Cl_2	2	0·121	0·0928	1·30
Bromine . .	Br_2	2	0·0555	0·0429	1·29
Carbon Dioxide	CO_2	3	0·2169	0·172	1·26
Marsh Gas . .	CH_4	5	0·5929	0·468	1·26
Ethene . . .	C_2H_4	6	0·4040	0·359	1·12
Ethyl Alcohol .	C_2H_6O	9	0·4534	0·410	1·11
Ether . . .	$C_4H_{10}O$	15	0·4797	0·453	1·05
Turpentine . .	$C_{10}H_{16}$	26	0·5061	0·491	1·03

It will be seen that the value of γ approximates more and more closely to unity as the number of atoms comprised in a molecule increases.

In the case of ordinary gases, such as oxygen, hydrogen, &c., we can obtain chemical evidence as to whether the molecules are monatomic, diatomic, &c. Thus, for instance, a molecule of HCl must at least be diatomic; and it is found that one volume of chlorine and one volume of hydrogen produce, when exploded, two volumes of hydrochloric acid gas. This can be explained, consistently with Avogadro's law, by the equation :—

$$H_2 + Cl_2 = 2HCl.$$

In the case of argon, helium, krypton, neon, and xenon, all of which appear to have no chemical affinities, the above evidence cannot be obtained. The value of γ may, however, be found from an experimental determination of the velocity of sound in the gas. (*See* Chap. XV. p. 329.)

It has been found in all these cases that γ has the value 1·666. This has been considered as sufficiently satisfactory evidence that the gases referred to are monatomic.

The theory discussed in the present chapter was first elaborated by J. J. Waterston in a paper communicated to the Royal Society in December 11, 1845. This paper was not printed till 1892, when it was found by Lord Rayleigh in the Archives of the Royal Society. In the meantime Clausius and others had gone over the same ground, and jointly elaborated an almost identical theory.

"The omission to publish [the above paper of Waterston's] was a misfortune which probably retarded the development of the subject by ten or fifteen years." (Lord Rayleigh, *Phil. Trans.* 1892. p. 2.)

SUMMARY TO CHAPTER XIII.

All substances are supposed to consist of molecules in rapid motion. In **solids** the motions occur about fixed positions. In **liquids** a molecule can move from place to place, but its progress is retarded by the occurrence of frequent collisions. In **gases** and vapours the molecules are more sparsely scattered, and consequently collisions are less frequent.

The pressure exerted by a gas is due to the reversal of the momenta of the gas molecules when these strike against the walls of the containing vessel.

The heat contained by a gas is equivalent to the sum of the kinetic energies of its constituent molecules.

Absolute Zero.—If the molecules of a gas were reduced to complete rest, no pressure would be exerted on the walls of the containing vessel. This would obviously correspond to the absolute zero of temperature as measured on a constant volume air thermometer.

The mean free path of a gas is equal to the mean distance traversed between successive collisions of a gas molecule.

Work Performed in Compressing a Gas Isothermally.—If the gas is contained in a cylinder, when the piston is moved inwards the molecules striking against it will rebound with augmented velocities. Thus the kinetic energy possessed by the molecules will be increased as the gas is compressed. This increase corresponds to the production of heat, and is equal to the work performed in compressing the gas. In order that compression should be performed isothermally, the molecules must give up this extra kinetic energy to the molecules composing the walls of the enclosure.

When a perfect gas expands isothermally, the external work performed is equivalent to the heat communicated to the gas by surrounding bodies during the expansion.

The method of graphically representing the work performed during the compression or expansion of a gas (shown in Fig. 140) should be remembered.

Internal Work of Expanding Gases.—If appreciable attractions are exerted between neighbouring molecules of a gas, work will be performed in separating these molecules during expansion.

Joule showed that the molecules of the permanent gases are so far removed from each other that the effects of their mutual attractions or repulsions are very small.

QUESTIONS ON CHAPTER XIII.

(1) What is the thermal evidence that the attraction between the molecules of the ordinary gases under standard conditions is small?

(2) Prove that the product of the density of a gas into the difference between its specific heats at constant pressure and at constant volume is the same for all perfect gases.

(3) Show how to obtain the gaseous laws of Boyle, Charles, and Avogadro from the principles of the kinetic theory of gases.

(4) Obtain a formula giving the value of J in terms of the pressure, temperature, and density of a mass of gas, and the difference between its two specific heats. What experiments are necessary to justify the assumption made in obtaining the formula?

(5) Explain why the specific heat of a gas at constant pressure is greater than the specific heat at constant volume.

CHAPTER XIV

VAN DER WAALS'S THEORY

Extension of the Dynamical Theory.—The dynamical theory, as developed in the preceding chapter, leads to theoretical equations for the isothermals of a gas, of the form

$$pv = \mathrm{RT}.$$

The curves corresponding to this relation between the pressure, volume, and temperature of a gas, possess the form of rectangular hyperbolas (Chap. V., p. 95). For temperatures far above the critical temperature (p. 207) of a substance, such curves agree fairly well with the results of accurate experiments. But for temperatures below the critical temperature, the isothermals have been found experimentally to possess a very different form. Starting with a quantity of vapour under a low pressure, we first obtain a curve AB (Fig. 142) approximating more or less closely to a rectangular hyperbola. At B an abrupt discontinuity occurs, corresponding to the commencement of liquefaction in part of the vapour. The isothermal now assumes the form of a straight line, parallel to the axis of volume. At C, another discontinuity occurs, corresponding to the complete liquefaction of the vapour. The remaining part CD of the isothermal, which represents the relation between the volume of the liquid and the pressure to which it is subjected, approximates to a straight line, slightly inclined to the axis of pressure.

In the present chapter will be given a brief account of an extension of the dynamical theory, due to J. D. Van der Waals, which leads to equations for the isothermals of a substance, of a form more nearly agreeing with the results of experiments. As an introduction we will consider certain theoretical conclusions, due to Prof. James Thomson, as to the true form of isothermals below the critical isothermal.

Prof. James Thomson's Hypothesis.—In 1871, Prof. James Thomson published an ingenious speculation, suggested by the form of the isothermals immediately above the critical isothermal, and based on the assumption that all transformations are essentially continuous. He suggested that the discontinuous part BC of the isothermal ABCD should be replaced by the continuous curve BEFGC. The whole of the isothermal ABEFGCD is now continuous, and nowhere exhibits any abrupt change of direction.

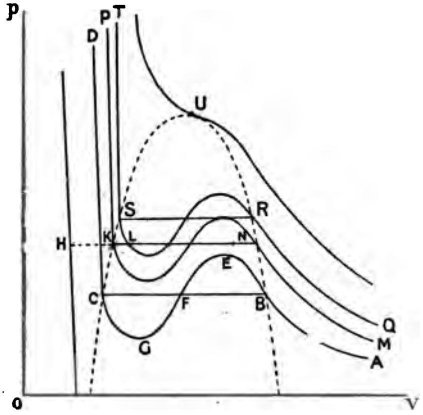

FIG. 142.—Theoretical form of isothermals for vapour and liquid, according to James Thomson.

Prof. James Thomson pointed out that if the isothermals of a substance below the critical temperature are assumed to possess the above shape, many well-known phenomena may be easily explained. In the first place, it is well known that a liquid may, under certain conditions, be heated to a temperature considerably above its boiling point, without ebullition occurring. Dufour, for instance, heated small drops of water, suspended in a mixture of oil of cloves and linseed oil, so proportioned as to have the same density as the water, and found that a temperature of 178° C. could be attained without ebullition of the water occurring. Now let us suppose that the point H, Fig. 142, represents the state of the water at a temperature somewhat below 100° C. From the nature of Dufour's experiment, this water was heated at constant pressure. It therefore passed through the states corresponding to successive points on the horizontal line HK. At K the water reached the extremity of the horizontal portion of the 100° isothermal MNKP. Under ordinary conditions ebullition would then have occurred, and the mixture of water and vapour would have remained at 100° C., the temperature corresponding to the isothermal MNKP, whilst the conditions corresponding to points on the straight line KN were successively attained. In the case in question, however, when the water had reached the point L on the line KN, it was at a temperature above 100° C., *i.e.*, it had reached a point on some higher isothermal, such as TSLRQ. It will be seen that if S and R are joined by a curved line similar in shape to CGFEB, an intersection of the curve with the straight line NK in the point L is possible.

Hence, according to Prof. James Thomson's hypothesis, those portions of the continuous isothermals similar to the part CG of the curve CGFEB, correspond to the condition of superheating.

Between the points G and E, the pressure increases with the volume. This would correspond to a state of instability, and the liquid would therefore suddenly be partially vaporised. This corresponds to the occurrence of the well-known phenomenon of bumping.

It may be shown, in a manner precisely similar to that employed above, that those portions of the continuous isothermals similar to the part BE of the curve CGFEB correspond to the supersaturation of a vapour. It is well known that a vessel filled with steam, and free from suspended dust particles, may be cooled to a temperature considerably below 100° C. without condensation occurring. On reaching a point similar to E, however, a sudden condensation, corresponding to the unstable portion EF of the curves, would ensue. Portions of the continuous isothermals similar to CG and BE can also be realised by carefully varying the volume and pressure of a liquid and its vapour whilst the temperature is kept constant.

Van der Waals's Theory.—Van der Waals proposed to introduce corrections into the equation obtained in the preceding chapter, so as to make allowance for the facts :—

(1) That in certain cases the effects due to the mutual attractions of neighbouring molecules cannot be neglected ; and (2) that the molecules of a substance are of finite dimensions.

The equation to be corrected is

$$pv = \text{RT}.$$

Correction for the Mutual Attractions of the Molecules.—In the interior of a mass of gas, the effects of the mutual attractions of neighbouring molecules may be neglected, since if a certain molecule is pulled in one direction by one molecule, it will, on an average, be pulled equally in an opposite direction by some other molecule or molecules. At the confines of the gas, however, the case is different. A molecule will be pulled back into the gas by the molecules behind it.

Hence, a molecule will strike the walls of the vessel whilst moving with a velocity less than the average velocity of the molecules within the gas. But, in obtaining the equations in the preceding chapter, the molecules striking the walls were supposed to possess the same mean square velocity as those in the interior of the gas. Hence, in our equations we must add to the pressure p, which is actually exerted on the walls of the vessel, a term equal to the diminution in the pressure produced by molecular attractions.

Considering the molecules at any time occupying a thin layer 1 sq. cm. in area near the confines of the gas, the attractive force on these will be proportional to the square of the density of the gas. For, if we double the number of molecules in the containing vessel there will be twice as many molecules to be pulled inwards, and twice as many within the range of molecular forces to pull them in that direction. Since the density of the gas will vary inversely as the volume which it occupies, we may state that the molecular attractions will give rise to a decrease of pressure varying inversely with the square of the volume of the gas. Hence, we may write the corrected pressure as

$$\left(p + \frac{a}{v^2}\right)$$

where a is a constant.

Correction for the Finite Size of Molecules.—Let CDEF, Fig. 143, represent a section of one of the elementary cubes in which the molecules of a gas have been assumed to move (*see* p. 291). If the diameter of a molecule is very small in comparison with the dimensions of one of these cubes, we may assume, as we did in the last chapter, that between successive rebounds from the face ED, the centre of gravity of the molecule moves through the distance AB + BA = 2AB. If, however, the diameter of a molecule is comparable with the dimensions of the cube in which it moves, we must take CC′, Fig. 143, as the mean intermolecular distance instead of AB, and the distance traversed between successive rebounds from the face ED will be equal to 2CC′ = 2 (AB – d) where d is the diameter of a molecule.* The effect of this practically amounts to a diminution of the volume v. Hence we must write $(v-b)$ instead of v in the equation

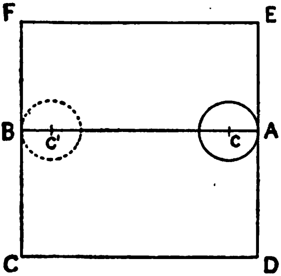

FIG. 143.—Illustration of the diminution of the mean free path, due to the finite size of molecules.

$$pv = \mathrm{RT}$$

where b is a constant.

According to Van der Waals, b is numerically equal to four times the actual volume of the molecules of the gas.

Hence, applying the corrections for molecular attraction and finite size of molecules, we obtain the equation

$$\left(p + \frac{a}{v^2}\right)\left(v - b\right) = \mathrm{RT}.$$

This equation may be plotted graphically. When T is taken smaller than a certain critical value, curves of the general form of ABEFGCD, Fig. 142, are obtained. For values of T above this critical value, curves are obtained agreeing in their general form with those obtained experimentally by Andrews for carbon dioxide at temperatures higher than 32·5° C.

The Critical Temperature.—Van der Waals's equation can be put into the following form, by multiplying by v^2 throughout, and arranging the terms in the order of the powers of v.

$$pv^3 - (bp + \mathrm{RT})v^2 + av - ab = 0$$

$$\therefore v^3 - \left(b + \frac{\mathrm{RT}}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0.$$

---

* The explanation given in the text is illustrative merely. For a full discussion of the question, see the author's *General Physics for Students*, p. 544.

For constant values of p and T, this becomes a cubic equation in v, which can consequently be satisfied by three root values of v. By a well-known theory, all three of these roots may be real, or one may be real and two imaginary.[1] Now, substituting constant values of p and T is equivalent to finding the intersection of the T° isothermal (say ABEFGCD, Fig. 142) with a straight line drawn parallel to the axis of volumes at a height p above the latter. CFB is part of such a line, and the volumes corresponding to the points C, F, and B will be equal to the three real roots of the above equation in v.

It may be seen that lines parallel to the axis of volumes, and at heights above that axis greater than that corresponding to the point E, or smaller than that corresponding to the point G, will only cut the curve ABEFGCD in one point. This corresponds to the case of one real and two imaginary roots to the above equation in v.

It will be noticed in Fig. 142 that the three points, in which an isothermal is cut by a straight line parallel to OV, become closer and closer together according as the isothermal approaches the critical isothermal. The critical isothermal itself will be intersected in three coincident points at U.

A cubic equation in v, possessing three equal roots, may be written in the form [2]

$$(v-\alpha)^3 = 0,$$

where α is the value of each of the equal roots.

Expanding this equation, and writing Van der Waals's general equation immediately below it, we have

$$v^3 - 3\alpha v^2 + 3\alpha^2 v - \alpha^3 = 0$$

$$v^3 - \left(b + \frac{\mathrm{RT}}{p}\right) v^2 + \frac{a}{p} v - \frac{ab}{p} = 0.$$

Equating the coefficients of equal powers of v in these two equations, we find that

$$3\alpha = b + \frac{\mathrm{RT}}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

$$3\alpha^2 = \frac{a}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

$$\alpha^3 = \frac{ab}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

---

[1] See Hall and Knight's *Higher Algebra*, Chap. XXXV.

[2] *Ibid.*

Combining (3) and (2), we have

$$\alpha = \left(\frac{a}{3p}\right)^{\frac{1}{2}} = \left(\frac{ab}{p}\right)^{\frac{1}{3}}.$$

Raising the two last members to the sixth power, we have

$$\left(\frac{a}{3p}\right)^{3} = \left(\frac{ab}{p}\right)^{2}.$$

$$\therefore \quad \frac{a^3}{27p^3} = \frac{a^2b^2}{p^2}.$$

$$\therefore \quad p = \frac{a}{27b^2} \quad . \quad . \quad . \quad (4).$$

This is the value of the critical pressure.

The critical volume, which will be equal to α, may be obtained by substituting in (2) the value of p found in (4). Then

$$3\alpha^2 = \frac{a}{p} = \frac{a \times 27b^2}{a} = 27b^2.$$

$$\therefore \quad \alpha^2 = 9b^2,$$

critical volume $= v_c = \alpha = 3b$ . . . . (5).

The critical temperature can be found by substituting in (1) the values of α and p, given by (4) and (5).

$$9b = b + \frac{R \times 27b^2}{a}T.$$

$$\therefore \quad T = \frac{8b \times a}{27Rb^2} = \frac{8}{27}\,\frac{a}{Rb}.$$

We can now summarise our results as follows :—

Critical temperature $= T_c = \frac{8}{27}\,\frac{a}{Rb}$

Critical volume $= v_c = 3b$

Critical pressure $= p_c = \frac{a}{27b^2}$

For carbon dioxide, Van der Waals obtained the values of a, b, and R in his general equation, by substituting corresponding values of p and v from Regnault's results on the compression of that gas at various temperatures. Taking unit pressure as the standard barometric pressure, and the unit volume as the space occupied by the gas at 0° C. and one atmosphere pressure, he found that

$$R = \frac{1\cdot00646}{273}$$
$$a = 0\cdot00874$$
$$b = 0\cdot0023$$

Substituting these values in the formula for the critical temperature, he obtained

$$T_c = \frac{8}{27} \cdot \frac{0\cdot00874 \times 273}{1\cdot0065 \times 0\cdot0023} = 305\cdot5.$$

$\therefore$ The critical temperature $= (305\cdot5 - 273) = 32\cdot5°$ C.

This result is in remarkably close agreement with the value of the critical temperature of carbon dioxide obtained experimentally by Andrews.

Corresponding States.—Instead of measuring the volume, pressure, and temperature of a substance in absolute units, we might express these quantities as fractions of the critical volume, pressure, and temperature of that substance.

Thus we might write

$$p = \lambda p_c$$
$$v = \mu v_c$$
$$T = \nu T_c.$$

Substituting these values in Van der Waals's general equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

we get $\left(\lambda p_c + \frac{a}{\mu^2 v_c^2}\right)(\mu v_c - b) = R\nu T_c.$

Substituting the values of p_c, v_c, and T_c, in terms of a, b, and R, we get

$$\left(\lambda\left(\frac{a}{27b^2}\right) + \frac{a}{9b^2\mu^2}\right)(3\mu b - b) = \nu R \frac{8a}{27Rb}.$$

Dividing this equation throughout by $\frac{a}{27b}$, we get

$$\left(\lambda + \frac{3}{\mu^2}\right)(3\mu - 1) = 8\nu \quad . \quad . \quad . \quad . \quad (a).$$

Van der Waals's general equation will have different forms for different gases, according to the values found experimentally for *a*, *b*, and R. The equation just found, however, is independent of *a*, *b*, and R, and will therefore serve to express the properties of one gas as well as another.

Hence, supposing Van der Waals's equation to accurately represent the properties of a particular gas, we see that if the pressures, volumes, and temperatures are measured in terms of the critical constants, an equation can be obtained which will represent the properties of all gases.

Dr. S. Young has found that the properties of the halogen derivatives of benzene are very approximately represented by the equation (*a*) above. For other substances, however, considerable divergences from the equation (*a*) were found.

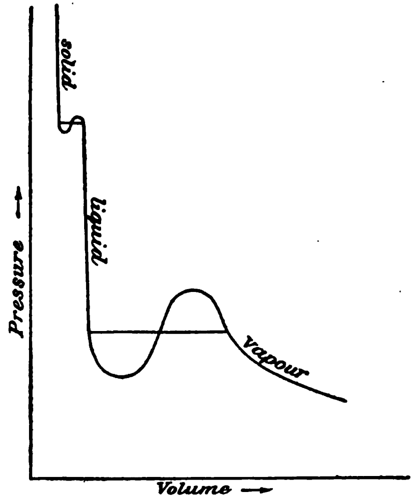

Fig. 144.—Theoretical form of isothermal for solid, liquid, and vapour.

Hence, Van der Waals's equation must be accepted as representing only a first approximation to the true form of the isothermals of a substance. This, indeed, is obvious when we remember that no explanation of solidification is afforded by this equation. The true form of an isothermal should be of the general form shown in Fig. 144.

Nevertheless, Van der Waals's investigation forms a most valuable contribution to the molecular theory. Clausius and others have since obtained formulæ which represent the properties of various substances to a closer degree of approximation. But these formulæ were obtained by introducing arbitrary constants which have no direct physical meaning.

SUMMARY TO CHAPTER XIV.

The dynamical theory of gases, as developed in Chapter XIII., has been found capable of explaining the properties of the so-called permanent gases at high temperatures. In order to account for the peculiarities of the isothermals of a substance capable of existing as a solid or liquid at the same temperature, additional assumptions must be made.

Professor James Thomson's Hypothesis.—The straight portions of the isothermals, corresponding to the occurrence of progressive liquefaction, may be replaced by curved lines as shown in Fig. 142. Certain parts of these curved lines obviously correspond to the phenomena of superheating of liquids and the supersaturation of vapours. Other parts of these curves indicate an unstable condition, which corresponds to boiling by bumping.

Van der Waals applied corrections to the equations obtained in Chapter XIII.,

(1) For the finite size of molecules.

(2) For the attraction exerted between neighbouring molecules when brought close to each other.

The resulting equations represent curves of the general form assumed by Professor James Thomson.

The critical temperature of carbon-dioxide, as calculated by Van der Waals from the results of Regnault's experiments, agrees closely with the value determined experimentally by Andrews.

In Van der Waals's investigation no account is given of solidification. Hence it can only be considered as a first approximation to a true molecular theory.

QUESTION ON CHAPTER XIV.

(1) Write a short essay on the characteristic equation of Van der Waals.

CHAPTER XV

ADIABATIC TRANSFORMATIONS

WE have already examined the relation existing between the pressure and volume of a gas when the temperature is kept constant. We have further found, in Chapter XIII., that heat is generated during the compression of a gas, and that this must be given up to surrounding bodies in order that the compression should be isothermal. Similarly, when work is performed by the expansion of a gas, cooling occurs unless heat is constantly supplied by surrounding bodies. Hence, generally, in order that isothermal transformations should be effected, the gas experimented on must be placed in thermal communication with surrounding bodies, which are supposed to be capable of communicating heat to, or absorbing it from, the gas, whilst their own temperatures remain constant.

Let us now consider what will happen if a quantity of gas is compressed in a vessel the walls of which are incapable of conducting heat. In this case, any heat which is generated in the gas cannot escape from it, so that its temperature will rise.

Adiabatic Transformation.—An adiabatic transformation may be defined as the result of any operations performed on a substance, subject to the condition that heat is neither communicated to, nor abstracted from, it by external bodies.

Adiabatic Curve.—We may represent the relation between the pressure and volume of a substance, when heat is neither communicated to, nor abstracted from, it by external bodies, by means of a curve. This is termed an adiabatic curve.

Certain characteristics of such a curve can be easily obtained. In the first case, it can be seen that *an adiabatic will be* *steeper than an isothermal curve.* For let OD, DA (Fig. 145), represent the initial volume and pressure of the gas. Then if the volume is diminished to OE under such conditions that the temperature of the gas remains constant, the corresponding pressure EF will be such that A and F lie on the isothermal BFAC. During the compression, the heat generated has been given up to surrounding bodies.

Now let us suppose that, the final volume OE of the gas being maintained constant, the heat removed during the isothermal compression is returned to the gas. The pressure will thus be increased, and we shall have the final state of the gas represented by the point G, EG being greater than EF. Hence the curve passing through A and G will be steeper than that passing through A and F.

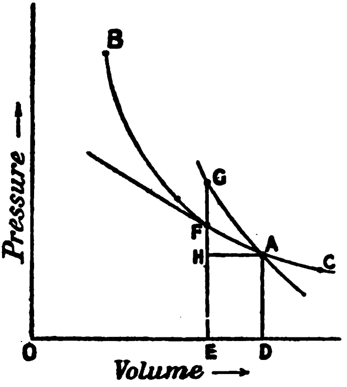

FIG. 145.—Slope of isothermal and adiabatic curves.

Slope of an Isothermal Curve.—Let us take any two points A, F, close to each other on an isothermal, and draw a straight line through them. Then, as A and F are taken closer to each other, the line joining them will approximate to the geometrical tangent to the isothermal at the point A.

The slope of the isothermal is most conveniently expressed in terms of the trigonometrical tangent of the angle which the line FA makes with OD, the axis of volumes.

Draw AH parallel to OD. Then if OD $= v$, DA $= p$, we may represent the diminution of volume in passing from A to F by dv, the increase of pressure being represented by dp. Hence AH $= dv$, OE $= (v - dv)$, HF $= dp$, EF $= (p + dp)$.

Let the angle FAH be denoted by θ. Then we have

$$\tan\theta = \frac{\text{HF}}{\text{AH}} = \frac{dp}{dv}.$$

If the gas referred to obeys Boyle's law, we have

$$pv = (p + dp)(v - dv) \qquad (1)$$

since the product of the pressure into the corresponding volume of the gas is constant.

$$\therefore\ pv = pv - pdv + vdp - dpdv \text{ from } (1)$$
$$\therefore\ vdp - pdv - dpdv = 0.$$

Now if A and F are very close together, AH($= dv$), and HF($= dp$) will be very small. In the above equation the two first terms are formed each from the product of two quantities, one of which is large, whilst the other is taken vanishingly small. The last term is formed from the product of two vanishingly small quantities. Hence the term $dpdv$ may be neglected in comparison with the remaining terms. Therefore,

$$vdp - pdv = 0$$
$$vdp = pdv$$
$$\frac{dp}{dv} = \frac{p}{v}$$
$$\therefore\ \tan \text{FAH} = \frac{dp}{dv} = \frac{p}{v} = \frac{\text{AD}}{\text{OD}}.$$

The Adiabatic Curves of a Perfect Gas.—In order to find an expression for the relation between the pressure and volume of a quantity of a perfect gas, when compressed or allowed to expand under adiabatic conditions, the following method may be followed :—

1. An expression is found for the tangent of the angle of slope GAH of the adiabatic curve.
2. A curve is selected which possesses this slope at all points in its course.

As a preliminary, the following problems must be solved :—

Problem.—To find the tangent of the angle of slope of the curve

$$pv^n = \text{constant}.$$

As before, we take two neighbouring points, the co-ordinates of which are respectively

$$p,\ v, \text{ and } (p + dp),\ (v - dv).$$

Then

$$\text{tangent of angle of slope} = \frac{dp}{dv}.$$

From the nature of the problem

$$(p + dp)(v - dv)^n = pv^n$$

$$(p + dp)v^n\left(1 - \frac{dv}{v}\right)^n = pv^n.$$

By the binomial theorem

$$\left(1 - \frac{dv}{v}\right)^n = 1 - n\frac{dv}{v} + \frac{n(n-1)}{1.2}\left(\frac{dv}{v}\right)^2 - \ldots.$$

When dv is small in comparison with v, powers of $\left(\frac{dv}{v}\right)$ higher than the first may be neglected. Therefore, to a close approximation

$$\left(1 - \frac{dv}{v}\right)^n = 1 - n\frac{dv}{v}.$$

Substituting this value, we get

$$(p + dp)v^n\left(1 - n\frac{dv}{v}\right) = pv^n.$$

$$\therefore\ pv^n + dp\,.\,v^n - ndv\,.\,v^{n-1}p - n\,.\,v^{n-1}dv\,.\,dp = pv^n.$$

Simplifying, and neglecting the term containing the product of dv and dp, we get

$$dp.v^n - ndv.v^{n-1}p = 0.$$

$$\therefore\ vdp - npdv = 0.$$

$$\therefore\ \frac{dp}{dv} = n\frac{p}{v}.$$

Thus the tangent of the angle of slope of the curve

$$pv^n = \text{constant}$$

is n times as great as the tangent of the angle of slope of the curve

$$pv = \text{constant}.$$

Conversely, if the tangent of the angle of the slope of a curve is given by

$$\frac{dp}{dv} = n\frac{p}{v}$$

the equation to the curve will be given by

$$pv^n = \text{constant}.$$

The Slope of an Adiabatic Curve.—Let us suppose that BC, Fig. 145, represents an isothermal for one gram of gas. Then, if AG is part of the adiabatic passing through A

$$\text{tangent of the angle of slope} = \frac{\text{HG}}{\text{HA}} = \frac{dp}{dv}.$$

It is required to determine the value of $\frac{dp}{dv}$ in terms of p and v.

According to the definition of an adiabatic curve, if the gas initially occupies the volume $v = \text{OD}$, Fig. 145, and is compressed till it occupies the volume $(v - dv) = \text{OE}$, gain or loss of heat from external sources being prevented, the final pressure of the gas will be equal to EG. The gas will then be at a higher temperature than that corresponding to the isothermal BC passing through A.

Let us suppose that, instead of performing the compression as above, the gas is first cooled at constant pressure till its condition corresponds to the point H; and that the volume is then maintained constant, whilst the heat which has been removed is returned to it. The pressure will increase till a condition corresponding to the point G is reached. Thus, instead of passing directly along AG, the point G has been reached by the broken path AH, HG.

Now the heat which must have been taken from the gas, the mass of which is one gram, in passing from A to H, is equal to $\sigma_p d\text{T}$, where σ_p is the specific heat of the gas at constant pressure, and $d\text{T}$ is the fall in temperature.

To pass from H to F at constant volume, the gas must be once more heated through $d\text{T}°$ C., since F is a point on the isothermal passing through A. The quantity of heat which must be communicated to it is equal to $\sigma_v d\text{T}$, where σ_v is its specific heat at constant volume.

But the actual quantity of heat taken from the gas in passing from A to H is equal to $\sigma_p d\text{T}$.

This heat when returned to the gas at H will increase its pressure by an amount equal to HG, where

$$\frac{\text{HG}}{\text{HF}} = \frac{\sigma_p d\text{T}}{\sigma_v d\text{T}} = \frac{\sigma_p}{\sigma_v}.$$

This follows from the facts that the rise of temperature of a given mass of gas, occupying a constant volume, is proportional to the quantity of heat communicated to it, and the resulting increase of pressure is proportional to the rise of temperature (p. 101).

$$\therefore \text{HG} = \frac{\sigma_p}{\sigma_v}\text{HF} = \gamma\text{HF},$$

$$\text{Where } \gamma = \frac{\sigma_p}{\sigma_v}.$$

$$\therefore \frac{dp}{dv} = \frac{\text{HG}}{\text{HA}} = \gamma\frac{\text{HF}}{\text{HA}} = \gamma\frac{p}{v},$$

since $\frac{\text{HF}}{\text{HA}}$ = the tangent of the angle of slope of the isothermal BC $= \frac{p}{v}$.

space may at pleasure be put into communication with, or shut off from, the atmosphere. The pressure of the enclosed gas is measured by the aid of a manometer M, whilst air can be forced into or withdrawn from C by way of a tube provided with an air-tight tap T. In order to thoroughly dry the enclosed gas, some strong sulphuric acid is poured into C.

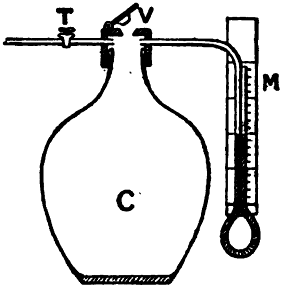

FIG. 147.—Apparatus for determining the ratio, γ, of the specific heats of a gas, by Clément and Desormes' method

The best liquid to use for the manometer is Fleuss pump oil. This gives off no vapour, whilst its density is low, and small variations of pressure can therefore easily be observed.

The experiment is performed as follows :—

1. The valve V is closed, and air is pumped into C till a pressure equivalent to about 30 cms. of water is indicated by the manometer. The stop-cock T is then closed. The density ρ of the Fleuss pump oil having been previously determined, the total pressure p_1 of the enclosed gas is given, in cms. of water, by

$$p_1 = P + h_1\rho,$$

where P is the barometric pressure in cms. of water, and h_1 is the difference in level of the surfaces of the oil in the two limbs of the manometer, measured in centimetres.

For some minutes after pumping has been discontinued, and the stop-cock T has been closed, the pressure indicated by the manometer slowly falls. This is due to the fact that the air, which was heated during its compression, is slowly attaining the temperature of the atmosphere. When the manometer indicates a stationary pressure, h_1 is observed.

2. The valve V is opened for one or two seconds and then closed. During the interval that it is open, the enclosed air expands till the pressure becomes equal to that of the surrounding atmosphere. If the vessel C is large, comparatively little heat will be communicated to the enclosed air during the expansion. Hence it may be assumed that the air has expanded adiabatically. Finally close the valve V.

3. At the instant when V is closed the surfaces of the oil in the two limbs of the manometer will be level with each other. After a short interval it will be noticed that the manometer indicates an increasing internal pressure. This is due to the fact that the enclosed air, which was cooled by expansion, is now attaining to the temperature of the surrounding air. When a stationary pressure is indicated, note the difference in level h_2 between the surface of the oil in the two limbs of the manometer. Then the final pressure p_2 of the enclosed air is equal to

$$P + \rho h_2.$$

Theory of the experiment.—During the time that the valve V (Fig. 147) was open, a certain quantity of air escaped into the atmosphere. Let us confine our attention, however, to a portion of the air which has remained inside C throughout the experiment. Let the volume of this air, under the initial pressure p_1, be equal to v_1. Then the initial condition of this air may be represented by the point C, Fig. 148, on the isothermal CEB, corresponding to the temperature of the surrounding air.

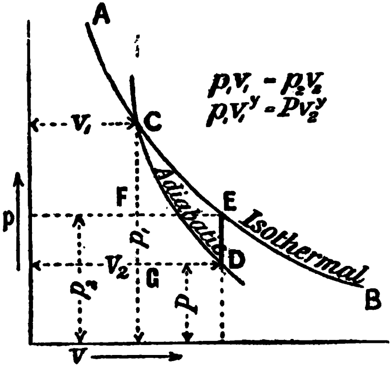

FIG. 148.—Graphic representation of operations performed in Clément and Desormes' experiment.

When the valve V was opened, this air expanded along the adiabatic CD till its pressure was equal to P, that of the surrounding atmosphere. At the instant when the valve was once more closed, the condition of the air corresponded to the point D.

The valve being closed, the volume of the contained air cannot alter appreciably, since the volume of air inclosed by the manometer is small, and therefore variations in the level of the surface of the oil produce negligible effects on the volume of air inclosed by C. Hence as the inclosed air attained to the temperature of the surrounding atmosphere, its pressure rose from D to E. The point E will therefore correspond to the final state of the air. Let its volume then be equal to v_2, whilst its observed pressure is equal to p_2.

When the manometer M (Fig. 147) contains oil, the pressure of the air inside C cannot be very much greater than the atmospheric pressure, since the manometer reads only to about 30 or 40 cms. of oil, which will correspond to less than 30 or 40 cms. of water, and the atmospheric pressure will amount to about 1000 cms. of water. Hence the arc CD (Fig. 148) of the adiabatic and the arc CE of the isothermal will be very small parts of these curves, and will approximate to short straight lines. From C draw a vertical line, *i.e.*, a line perpendicular to the axis of volume; and from E and D draw lines perpendicular to the axis of pressure, cutting the vertical through C in the points F and G. Then the angle of slope of the adiabatic is CDG, and the tangent of this angle is CG/GD. The angle of slope of the isothermal is CEF, and the tangent of this angle is CF/FE=CF/GD. Therefore (p. 319)

$$\gamma = \frac{\textit{tan. angle of slope of adiabatic}}{\textit{tan. angle of slope of isothermal}} = \frac{\frac{\mathrm{CG}}{\mathrm{GD}}}{\frac{\mathrm{CF}}{\mathrm{GD}}} = \frac{\mathrm{CG}}{\mathrm{CF}}.$$

Now $\mathrm{CG} = p_1 - \mathrm{P} = \rho h_1$, and $\mathrm{CF} = p_1 - p_2 = \rho(h_1 - h_2)$; thus

$$\gamma = \frac{\rho h_1}{\rho(h_1 - h_2)} = \frac{h_1}{h_1 - h_2}.$$

When a manometer containing mercury is used the arcs CD and CE will no longer approximate to straight lines, and consequently a more complicated procedure is necessary for calculating the value of γ from the observed manometer readings. This procedure will now be explained.

Since C and E are on an isothermal, we have

$$p_1 v_1 = p_2 v_2, \quad \therefore \frac{v_2}{v_1} = \frac{p_1}{p_2} \quad . \quad . \quad . \quad . \quad (a).$$

Since C and D are on an adiabatic, we have

$$p_1 v_1^{\gamma} = \mathrm{P} v_2^{\gamma}, \quad \therefore \left(\frac{v_2}{v_1}\right)^{\gamma} = \frac{p_1}{\mathrm{P}} \quad . \quad . \quad . \quad (b).$$

Substituting in (*b*) the value of $\frac{v_2}{v_1}$ obtained from (*a*), we get

$$\left(\frac{p_1}{p_2}\right)^{\gamma} = \frac{p_1}{\mathrm{P}}.$$

Taking logarithms of both sides of this equation, we get

$$\gamma(\log p_1 - \log p_2) = \log p_1 - \log P.$$

$$\therefore\ \gamma = \frac{\log p_1 - \log P}{\log p_1 - \log p_2}.$$

Determination of γ from the Velocity of Sound.—When a regular succession of compressions and rarefactions are propagated, at sufficiently short intervals, through the air, the ear becomes conscious of a musical note. We will now obtain an expression for the velocity with which a compression is propagated through a gas. This will be equal to the velocity of sound in the gas.

Let us suppose that we are provided with a very long tube, the internal sectional area of which is equal to 1 sq. cm. Part of such a tube is represented by AB, Fig. 149. Let us further suppose that this tube is fitted with an air-tight piston P, capable of moving along AB without friction. Our calculations will be simplified if we assume the mass of this piston and its attachments to be so small as to be negligible.

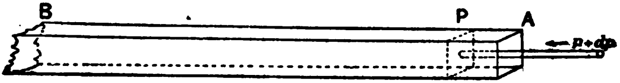

FIG. 149.—Tube with movable piston.

Let p be the atmospheric pressure. Then, if the tube is open at its other end, the force on either side of the piston will be equal to p dynes.

Let the force pressing the piston into the tube be increased to $(p + dp)$ dynes. The piston will commence to move inwards. We must now study the effects produced on the air inclosed in the tube.

The first effect will be to compress the layer of air immediately in contact with the piston. When this has been so far compressed that its pressure amounts to $p + dp$, no further compression will take place in it; it will then merely serve to transmit the pressure $p + dp$ to the next layer, which will be compressed in its turn, and so on.

But during the compression of any layer, all the layers which have been previously compressed must move in the direction from A to B through the distance by which the layer in question is compressed.

Let us suppose that, if the pressure of the air contained in AB were increased from p to $p + dp$, one cubic centimetre of the air would have its volume diminished by dv. Then, if V cms. per second is the velocity with which a compression is propagated along AB, it is plain that V c.cs. will be compressed per second, since the sectional area of the tube is one square centimetre. Hence, the piston will move inwards at a uniform rate of Vdv cms. per second; and as the air already compressed simply serves to transmit the pressure to that which is uncompressed, the whole of the air which has been compressed will move forward with the same velocity as the piston, *i.e.*, Vdv cms. per second. Therefore, in each second V c.cs. of gas will be set in motion with a velocity of Vdv cms. per second. Let ρ be the density of the air at a pressure of p dynes per sq. cm. Then during each second, Vρ grammes of air will be set in motion with a velocity of Vdv cms. per second.

∴ Kinetic energy communicated to the air in each second $= \frac{1}{2}\mathrm{V}\rho \times (\mathrm{V}dv)^2$ ergs.

We must next find the work performed in compressing the air during one second. This will be equal to the average pressure of the air during the compression, multiplied by the amount by which the volume of the air is decreased (p. 297).

Initial pressure of air $= p$.
Final ,, ,, $= p + dp$.

∴ Average pressure during compression $= p + \frac{1}{2}dp$.

In one second V c.cs. are compressed by Vdv c.cs.

∴ Work performed during each second in compressing the air within the tube $= (p + \frac{1}{2}dp)\mathrm{V}dv$ ergs.

Now, the kinetic energy communicated during one second to the air within the tube, *plus* the work performed in compressing the air, is equal to the work performed by the agent moving the piston inwards. This latter is equal to the uniform pressure $(p + dp)$, tending to force the piston inwards, multiplied by the distance Vdv through which the piston moves in a second. Hence finally we have: Work performed by agent = kinetic energy communicated to the air per second + work performed in compressing air per second.

$$(p + dp)(\mathrm{V}dv) = \tfrac{1}{2}\mathrm{V}\rho(\mathrm{V}dv)^2 + (p + \tfrac{1}{2}dp)\mathrm{V}dv.$$

$$\therefore\ \tfrac{1}{2}dp \,.\, \mathrm{V}dv = \tfrac{1}{2}\mathrm{V}\rho(\mathrm{V}dv)^2$$

$$dp = \mathrm{V}^2\rho dv$$

$$\mathrm{V}^2 = \frac{dp}{\rho dv}$$

$$\left.\begin{array}{l}\text{Velocity with which a com-}\\ \text{pression is transmitted . .}\end{array}\right\} = \mathrm{V} = \sqrt{\frac{dp}{\rho dv}}.$$

The quantity $\frac{dp}{\frac{dv}{v}}$, which represents the ratio of a small increase of pressure, to the corresponding diminution of volume *experienced by* 1 *c.c. of air*, is termed the volume elasticity of the air. Writing this as η, we have

$$\text{Velocity of sound in air} = \sqrt{\frac{\eta}{\rho}} = \sqrt{\frac{\text{Elasticity}}{\text{Density}}}.$$

To Calculate the Isothermal Elasticity of Air.—In this case we must determine the ratio of a small increase of pressure to the corresponding diminution of volume produced in 1 c.c. of air, when the latter is kept at a uniform temperature.

Let p be the initial pressure, and v the initial volume occupied by a certain quantity of air. Then, by Boyle's Law, if an increase of pressure dp produces a diminution of dv in the v c.cs. of air, we have

$$\begin{aligned} pv &= (p + dp)(v - dv) \\ &= pv - pdv + vdp - dpdv. \end{aligned}$$

Subtracting pv from both sides of this equation, and neglecting the product of the two small quantities dp and dv, in comparison with the remaining terms, we have

$$vdp = pdv.$$

$$\therefore \frac{dp}{\frac{dv}{v}} = p.$$

Remembering that $\frac{dv}{v}$ is equal to the diminution produced in 1 c.c. of air when the pressure is increased from p to $p + dp$, we see that

$$\text{Isothermal elasticity} = \frac{dp}{\frac{dv}{v}} = p = \text{initial pressure of the air.}$$

Newton was the first to obtain an expression for the velocity of sound in the form

$$V = \sqrt{\frac{\text{Elasticity}}{\text{Density}}}.$$

He thought that the isothermal elasticity should be used.

Now under a pressure of 760 mm. of mercury, 1 c.c. of air at 0° C. weighs ·001293 grams.

$\therefore$ Density of air, under these conditions = ·001293 grams per c.c.

Elasticity of air = pressure of air (in dynes) $= 76 \times 13{\cdot}6 \times 981$
$= 1{\cdot}014 \times 10^6$ dynes.

$\therefore$ Velocity of sound, on Newton's Hypothesis $= \sqrt{\dfrac{1{\cdot}014 \times 10^6}{{\cdot}001293}}$
= 28,000 cms. per second.

The actual velocity of sound in air at 0° C., as determined experimentally, is equal to 33,180 cms. per second, a value much larger than that obtained theoretically by Newton.

Adiabatic Elasticity of Air.—Laplace pointed out that the compressions and rarefactions, which occur when sounds are being transmitted must be produced under adiabatic conditions. Thus, in the tube previously considered, since a compression travels at the rate of 33,180 cms. per second, the time occupied in compressing each cubic centimetre will be less than a thirty-thousandth of a second. In this short interval of time no opportunity will be afforded for the air to give up the heat produced by compression; indeed, no more perfect realisation of adiabatic conditions could easily be imagined. Therefore, we must find the value of the adiabatic volume elasticity to substitute in Newton's formula:—

$$V = \sqrt{\frac{\text{Volume elasticity}}{\text{Density}}}.$$

Consider what happens to a volume v of air, when the initial pressure p is increased to $p + dp$ under adiabatic conditions.

We have

$$pv^\gamma = (p + dp)(v - dv)^\gamma = (p + dp)v^\gamma\left(1 - \frac{dv}{v}\right)^\gamma$$

$$= (p + dp)v^\gamma\left(1 - \gamma\frac{dv}{v} + \text{terms that may be neglected}\right).$$

$$\therefore pv^\gamma = pv^\gamma - \gamma pv^{\gamma-1}dv + dpv^\gamma - \gamma v^{\gamma-1}dpdv.$$

Subtracting pv^γ from both sides or this equation, and neglecting the term $\gamma v^{\gamma-1}dpdv$, which comprises the product of the small quantities dp and dv, we have

$$v^\gamma\, dp = \gamma pv^{\gamma-1}dv.$$
$$vdp = \gamma pdv.$$
$$\frac{dp}{\frac{dv}{v}} = \gamma p.$$

$\dfrac{dp}{\frac{dv}{v}}$ obviously represents the elasticity of the air. Hence, adiabatic elasticity of air $= \gamma p$.

Substituting this value of η in Newton's formula, we get, if $\gamma = 1{\cdot}40$

$$\text{Velocity of sound in air} = V \sqrt{\frac{\gamma p}{\rho}} = \sqrt{\frac{1{\cdot}40 \times 1{\cdot}014 \times 10^6}{{\cdot}001293}}$$

$$= 33{,}130 \text{ cms. per second.}$$

Determination of γ from the Velocity of Sound.—If the density ρ of any gas, when subjected to a pressure p, is known, and the velocity of sound in the gas can be determined, the value of γ can be obtained from the equation

$$V = \sqrt{\frac{\gamma p}{\rho}}$$

$$\therefore \gamma = \frac{\rho}{p} V^2.$$

Magnitude of the Compressions transmitted in a train of Sound Waves.—When a musical note is sounded, a number of compressions, alternating with rarefactions, are propagated through the air. Lord Rayleigh estimates that at a point in the air where a note, corresponding to the middle C of the piano (256 complete vibrations per second), is just audible, the variations in the pressure amount to no more than

$$\pm 6 \times 10^{-9} \text{ atmosphere.}$$

This is a variation of pressure far smaller than can be directly measured by any known means.

Adiabatic Expansion of a Saturated Vapour.—The general form of the isothermals of a substance, for temperatures immediately below the critical temperature, is indicated in Fig. 150 (*see* also p. 207). On the straight parts AB, CD, of these isothermals, the substance exists partly as liquid and partly as saturated vapour. At the points A, C, &c., on the dotted line ACK, passing through the extremities of the straight portions of the isothermals, the substance is wholly in the state of saturated vapour.

Let the isothermals in Fig. 150 be considered to refer to one gram of a particular substance, and let the curve passing through A refer to T°, and that passing through C to (T + 1)°. Then, in order that one gram of the substance should remain in the state of saturated vapour whilst it is heated from T° to (T + 1)°, a transformation along the dotted line AC must be effected.

Now it may be shown by the aid of reasoning similar to that employed on p. 297, that during this transformation, which involves an alteration of volume from O*a* to O*c*, an amount of work equal to the area A*ac*CA must be performed. This work will be transformed into heat in the vapour, and it may happen that the heat thus produced is itself sufficient to raise the temperature of the vapour from T° to (T + 1)°. In this case no heat need be communicated to the vapour from external sources. Consequently we might say that the specific heat of the saturated vapour had a zero value.

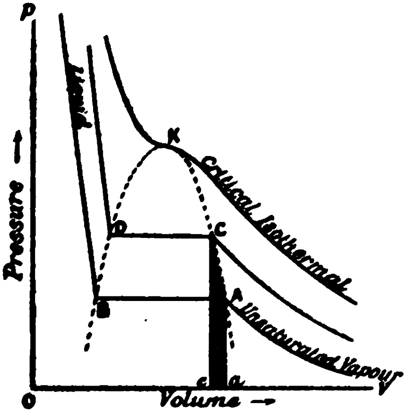

FIG. 150.—The shaded portion of this diagram corresponds to the work that must be performed in order that a vapour should remain saturated when its temperature is raised.

It may even happen that more heat is developed during the transformation from A to C than is required to heat the vapour from T to (T + 1)°. In this case heat must be removed from the substance as it passes from A to C. We should then have the peculiar phenomenon of a substance parting with heat as its temperature is raised, and absorbing heat as its temperature falls. We might then say that the saturated vapour in question possessed a negative specific heat.

If the heat equivalent of the work corresponding to the area A*ac*CA is not sufficient to raise the temperature of the vapour from T to (T + 1)°, heat must be supplied from external sources during the above transformation, and the saturated vapour possesses a positive specific heat.

It may easily be seen that a saturated vapour will possess a specific heat of zero value when the adiabatic through A coincides with the line AC. If the adiabatic through A slopes more steeply than AC, the saturated vapour will possess a negative specific heat, whilst a positive specific heat will correspond to an adiabatic sloping less steeply than AC.

Specific Heat of Saturated Steam.—The specific heat of saturated steam is negative at ordinary temperatures.[1]

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[1] See Table on p. 467 at end of book.

Hence, if a mixture of steam and water is compressed under adiabatic conditions, some of the water will be converted into steam. On the other hand, if saturated steam is allowed to expand, part of it will be converted into water (see also p. 240).

Hirn's Experiments.—Hirn inclosed a quantity of steam, under a pressure of 5 atmospheres, in a long copper cylinder with glass ends. Initially the steam was perfectly transparent; but on opening a valve, and allowing some of the steam to escape, that which remained in the cylinder became partially condensed, forming an opaque cloud.

Specific Heat of Saturated Ether Vapour.—Saturated ether vapour possesses a positive specific heat. Hence, if a quantity of saturated ether vapour is compressed, a partial condensation will occur, whilst if the volume of a vessel containing a quantity of ether and its saturated vapour is suddenly enlarged, some of the liquid ether will be converted into vapour.

SUMMARY TO CHAPTER XV.

An Adiabatic transformation may be defined as the result of any operations performed on a substance, subject to the condition that heat is neither communicated to, nor abstracted from, it by external bodies.

Adiabatic Curve.—A curve representing the relation between the pressure and volume of a substance when heat is neither communicated to, nor abstracted from, it by external bodies, is termed an adiabatic curve. An adiabatic curve of a gas has a steeper slope at any point than the isothermal cutting it at that point.

The equation to the adiabatic of a perfect gas is given by

$$p\,v^{\gamma} = \text{constant},$$

where γ is the ratio of the constant pressure and constant volume specific heats of the gas.

The value of γ may be experimentally determined—

(1) From direct measurements of the constant pressure and constant volume specific heats of a gas (see pages 156 to 161).

(2) By Clément and Desormes' method. A quantity of compressed (or rarefied) gas is put for a few moments in communication with the atmosphere, so that its pressure may sink (or rise) adiabatically to the atmospheric pressure. During this process the temperature of the gas falls (or rises), and after the gas has been shut off from the atmosphere the pressure increases (or decreases) until the temperature of the atmosphere is once more attained.

(3) From the velocity of sound. The velocity of sound in gas is equal to

$$\sqrt{\frac{\eta}{\rho}}$$

where η = the adiabatic elasticity of the gas, *i.e.*, the ratio of a small increase of pressure to the corresponding diminution of volume produced in each c.c. of the gas, when the compression is performed adiabatically.

ρ = the density (mass of unit volume) of the gas at the initial temperature and pressure.

The adiabatic elasticity of a gas is equal to the product of γ (the ratio of the specific heats of the gas) into the pressure of the gas.

Specific Heat of Saturated Vapours.—When the temperature of a mass of saturated vapour is raised, the vapour must be compressed in order that it should remain saturated. During this process work must be performed on the vapour, and the heat thus produced may be sufficient (or more than sufficient) to produce the requisite rise of temperature.

In the latter case heat will be given out by the saturated vapour as its temperature is raised, and consequently its specific heat is said to be negative.

Saturated steam possesses a negative specific heat. When it is allowed to expand adiabatically a partial condensation occurs.

QUESTIONS ON CHAPTER XV.

(1) Prove the law connecting the temperature and volume of a mass of perfect gas undergoing adiabatic compression.

How many degress will dry air at 15° C. and normal pressure rise if it be suddenly compressed to one-fourth its volume?

Take the ratio of the specific heats as 1·4.

(2) Show how to find the specific heat of a gas at constant volume from a knowledge of its value at constant pressure, and of the velocity of sound. Explain further how Joule's equivalent may be found from the values of the two specific heats.

(3) Explain the difference between the adiabatic and the isothermal elasticities of a substance, and show how to determine the ratio of these two elasticities for common air experimentally.

(4) What are adiabatic and isothermal changes?

Show on the indicator diagram the general course of the adiabatic and isothermal lines for water substance which is initially in the vaporous condition not far from its condensing point, and show that condensation may be produced either by adiabatic expansion or isothermal compression.

CHAPTER XVI

CARNOT'S CYCLE AND THE SECOND LAW OF THERMODYNAMICS

An Ideal Heat Engine.—All heat engines exhibit the characteristic that heat disappears during the performance of work. Thus, in Hirn's experiment (p. 283) it was found that during a given time the heat entering the cylinder of a steam engine was greater than that carried away by the waste steam, the excess being proportional to the work performed by the engine.

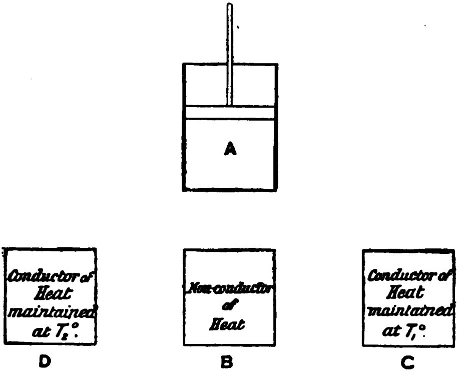
A
Conductor of Heat maintained at T_2°.
Non-conductor of Heat
Conductor of Heat maintained at T_1°.
D
B
C

FIG. 151.—Diagrammatic representation of an ideal heat engine.

On the other hand, heat engines differ considerably one from another in details of their construction. In many cases these differences are purely of a mechanical nature, and consequently do not concern us in the study of heat. Thus, the commercial efficiency of an engine depends on the accuracy with which the various parts have been shaped and put together, and will vary with the system of lubrication employed, together with many other circumstances of a like nature. It is therefore advisable, in studying the purely thermal side of the subject, to select some simple form of engine, so that our attention may be concentrated on the essential features of the thermal operations. In speaking of a "simple form of engine," it must be understood that the simplicity lies in the theory of the operations, rather than in the method by which these operations could be carried out in practice.

Let us suppose, then, that we are provided with a cylinder A, furnished with an air tight and frictionless piston, and filled with a substance which we may at first consider to be a gas. For simplicity we will suppose that the piston and sides of the cylinder are impermeable to heat, but that the bottom of the cylinder is a perfect conductor. Thus, if the cylinder is placed on a non-conducting base, any alterations which occur in the inclosed gas will be subject to adiabatic conditions. On the other hand, heat may be communicated to the inclosed gas by standing the cylinder on a conducting base maintained at a suitable temperature.

Cyclical Operations.—Let us suppose that the isothermals for a certain quantity of a substance have been determined and plotted in the manner previously described, (*see*, for instance, pp. 98 and 207). Then it is clear that any point in the quadrant lying between the axes of pressure and volume will correspond to a definite condition of the substance; *i.e.* the substance will be subjected to a certain pressure, will occupy a certain volume, and will be at a definite temperature.

It is equally clear that if any thermal transformation be effected, the various stages of that transformation may be represented by points on a curve drawn in the quadrant lying between the above axes.

As a particular instance of such transformation, we may suppose that the substance is finally brought back to its initial condition. In this case the various stages of the transformation may be represented by a closed curve such, for instance, as ABCDEFA, Fig. 152. A definite temperature, pressure, and volume of the substance will correspond to each point on the curve. We may imagine a quantity of some substance, initially in a condition represented by A, to successively pass through the conditions corresponding to the points BCDEFA along the given curve. Then the substance is said to have been subjected to a cycle of operations, or to have traversed the cycle ABCDEFA.

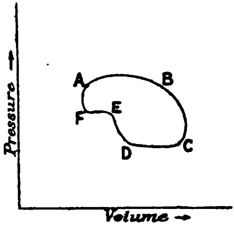

FIG. 152.—Graphic representation of a complete cycle of operations.

Reversible Cycles.—If a substance can be caused to traverse a cycle either in the order ABCDEFA, or in the order AFEDCBA, Fig. 152, the thermal actions at all points being reversed when the cycle is traversed in a reverse direction, the cycle is said to be reversible.

Internal Energy.—In certain cases, heat may be used up by a substance in the performance of internal work. A familiar instance is afforded by the heat absorbed during a change of state. Thus, during the conversion of one gram of water at 100° C. into steam at the same temperature, 537 therms. are absorbed. When a quantity of heat, equivalent to the external work performed during the expansion which occurs, has been subtracted from the total latent heat of steam, we are still left with a considerable quantity of heat which has disappeared (p. 369).

From the first law of thermodynamics, this heat must have been used up during the performance of work. We are thus led to the conclusion that internal work is performed on the water during its conversion into steam. In the performance of this work the potential energy of the molecules has been in some manner increased. This increase of potential energy may be reconverted into heat by allowing the steam to condense.

Internal work would also be performed during the expansion of a gas, if attractive forces were exerted between neighbouring molecules.

In traversing a complete cycle the substance is finally brought back to its initial condition. Thus, the potential energy possessed by the molecules will have the same value at the end, as at the beginning, of the cycle. Consequently, in estimating the amount of work performed *during a cycle*, any changes which may have occurred in the internal energy of the substance may be left out of account. These changes of energy must cancel each other.

Carnot's Reversible Cycle.—We have already investigated some of the most important properties of two sets of curves which can be drawn in the quadrant lying between the axes of pressure and volume. We have learnt to call these curves *isothermals* and *adiabatics* respectively. The condition of a substance during an isothermal transformation is defined by the restriction that its temperature must remain constant. In passing along an adiabatic, the condition to be complied with is that no heat shall be communicated to or abstracted from the substance by external bodies.

The above conditions are the simplest imaginable, and therefore a cycle of operation which involves only isothermal and adiabatic transformations will be of a simpler character, than one represented by an arbitrary curve such as that given in Fig. 152. Such a cycle is therefore often termed *a simple cycle.*

Referring once more to Fig. 151, let us suppose that we are provided with the cylinder A containing a quantity of a perfect gas. In this case no internal work is performed during expansions and compressions. Let us further suppose that in addition to the non-conducting stand B, we are provided with the two conducting stands C and D, maintained at the absolute temperatures $T_1°$ and $T_2°$ respectively, T_1 being greater than T_2. The temperatures of these stands are supposed not to change when heat is taken from or added to them.

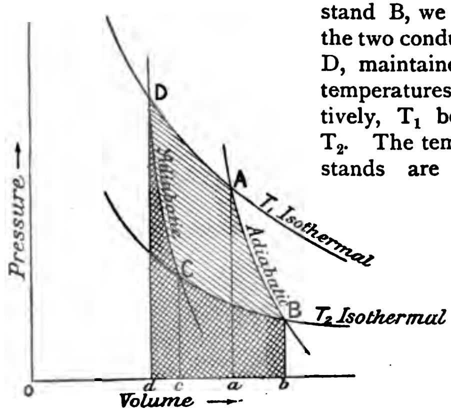

FIG. 153.—Graphic representation of Carnot's Cycle.

Let us suppose that the gas in A is initially at the temperature T_1 and occupies a volume equal to O*a*, Fig. 153, under a pressure equal to *a*A. Then the initial condition of the gas is represented by the point A.

The following operations may now be performed.

(A) Place the cylinder on the non-conducting stand B, and allow the gas to expand adiabatically till its temperature falls to T_2°.

The adiabatic line AB will be traversed from A to B, and during the expansion, a certain amount of external work, equal to the area AB*ba*, will be performed (p. 297). This work might be utilised in raising weights, or in driving machinery. The area AB*ba* has been shaded downwards from left to right, in order to indicate that the work has been performed *by the gas on external bodies.*

(B) Place the cylinder on the conducting stand which is maintained at a temperature T_2, and force the piston in till the volume of this contained gas has been reduced from O*b* to O*c*. It is supposed that the gas remains during this operation at the uniform temperature T_2. Hence, in passing from B to C, the isothermal BC will be traversed.

A certain amount of work equal to the area BC*cb* has been performed by external agency during this operation. This work has been converted into heat, which has been communicated to the stand maintained at the temperature T_2. Let us suppose that the total amount of heat thus rejected is equal to Q_2.

The area BC*cb* has been shaded downwards from right to left to indicate that work has been performed *by external agency on the gas.*

(C) Place the cylinder on the non-conducting stand B, and force the piston inwards, thus compressing the inclosed gas adiabatically till its temperature rises to T_1. The adiabatic CD will be traversed from C to D, and an amount of work equal to the area CD*dc* will be performed *on the gas by external agency.* This area is accordingly shaded downwards from right to left.

(D) Place the cylinder on the conducting stand C, which is maintained at the temperature T_1, and allow the gas to expand till it attains its original volume. The isothermal DA will be traversed from D to A, and an amount of external work equal to the area DA*ad* will be performed *by the gas.* Hence the area DA*ad* has been shaded downwards from left to right. In order that the temperature of the gas may be maintained at T_1, a quantity of heat equivalent to the total work performed must have been communicated to it from the stand C.

Let Q_1 be the heat communicated to the gas during this last operation.

Certain parts of the diagram have become cross-hatched. These parts represent work first performed *on the gas by external agency*, and subsequently performed *by the gas on external bodies.* In the complete cycle these quantities of work cancel each other (p. 264). On the other hand, the area inclosed by the figure ABCD is shaded only from left to right. This area, therefore, represents the net amount of external work performed *by the gas* whilst the cycle ABCD was traversed.

The results of the cycle can now be summarised as follows :—

1. The gas was initially in the condition represented by the point A, and is finally brought back to the same condition.

2. A quantity Q_1 of heat was absorbed whilst the gas was at the temperature T_1.

3. A quantity Q_2 of heat was given up by the gas whilst at a temperature T_2.

4. A net amount of external work equal to the area ABCD, has been performed *by the gas.*

From the *First Law of Thermodynamics*, the net amount of work performed during the cycle must be equal to the heat which has disappeared. Hence the area ABCD must be dynamically equivalent to (Q_1-Q_2).

The Cycle described above is Reversible.—Thus, starting at A, compress the gas isothermally till its volume is diminished to O*d*. The isothermal AD is thus traversed from A to D, and a quantity of work equal to the area AD*da* is perfermed *by external agency on the gas.* A quantity of heat Q_1 is thus given out by the gas.

Allow the gas to expend adiabatically till its temperature falls to T_2. A quantity of work equal to the area DC*cd* is thus performed *by the gas.*

Now allow the gas to expand isothermally from C to B. A quantity of work equal to the area CB*bc* is performed *by the gas*, and a quantity of heat equal to Q_2 is absorbed.

Finally, compress the gas adiabatically from B to A. An amount of work equal to the area BA*ab* will be performed *by external agency on the gas.*

Fig. 153 will represent the operations performed, if we now consider portions shaded downwards from left to right to represent work performed *by external agency on the gas*, portions shaded from right to left representing *external work performed by the gas.*

The result may be summarised as follows :—

1A. The gas was initially in the condition represented by the point A, and is finally brought back to the same condition.

2A. A quantity Q_1 of heat was given up by the gas whilst at an absolute temperature T_1.

3A. A quantity Q_2 of heat was absorbed by the gas whilst at a temperature T_2.

4A. A net amount of work, equal to the area ABCD has been performed *by external agency on the gas.*

From the *First Law of Thermodynamics*, the heat $(Q_1—Q_2)$ which has made its appearance, is equivalent to the work performed on the gas by external agency during this series of operations, *i.e.*, to the area ABCD.

Comparing the results obtained above, we see that in the case where external work was performed, heat was absorbed at a temperature T_1, and part of it was given up at a lower temperature T_2. Hence in this case, heat flows from a hot body to one at a lower temperature. On the other hand, when heat was absorbed at T_2, and given out at a higher temperature T_1, work was necessarily performed by external agency on the gas.

The Second Law of Thermodynamics.—According to Clausius, this may be stated as follows :—

It is impossible for a self-acting machine, unaided by any external agency, to convey heat from a body at a low to one at a higher temperature; or heat cannot of itself (that is, without the performance of work by some external agency) pass from a cold to a warmer body.

This law represents the result of universal experience with regard to heat engines and the general phenomena attending the transference of heat.

It must be clearly understood that it only applies to cyclical operations *i.e.*, when the working substance is in the end brought back to its initial condition.

Passage of heat from a cold to a warmer body.—Let us suppose that we are provided with two cylinders A and B, each fitted with an air-tight and frictionless piston, the pistons and walls of the cylinders being non-conductors of heat

Let the air in A be initially at a higher pressure but at a lower temperature than that in B. Then if the pistons are connected in a suitable manner, the air in A may be allowed to expand and compress the air in B. Both operations will be performed under adiabatic conditions, and therefore the air in A will be cooled, and that in B will be heated. Further, as the work performed *by* the air in A is equal to the work performed *on* the air in B, the amount of heat which disappears in A will be equal to that generated in B. Hence heat will disappear from a cold body A, and reappear in a warmer one B.

It must be noticed, however, that at the end of the experiment the condition of the air in either cylinder will differ from its initial condition. Hence, no breach of the Second Law of Thermodynamics is involved.

The following experiment, which at first sight seems to contradict the above law, is capable of a somewhat similar explanation.

EXPT. 64.—Make a saturated aqueous solution of calcium chloride, and having placed a thermometer in it, heat the solution by the aid of a Bunsen flame to about 95° C. Now pass steam into the solution, and note the temperature to which it rises. It will be found that a temperature of 109—112° C. will be finally attained.

In this experiment, heat passes from steam at 100° C. to the solution which is at a higher temperature.

During the experiment, steam is condensed in the solution, so that its initial and final conditions will be different. The strength of the solution is, in fact, progressively weakened. Hence this case is outside the Second Law of Thermodynamics.

The actual explanation of the experiment is somewhat as follows. Calcium chloride is a highly hygroscopic substance; consequently when steam is passed into the strong solution, part of it is condensed to form a loose chemical combination with the calcium chloride. But for every gram of steam condensed, about 536 therms are given up, so that the temperature of the solution rises. The temperature will continue to rise till the boiling point of the solution is reached, when no further change will take place.

Compare the results of the above experiment with those obtained when water and strong sulphuric acid, initially at the same temperature, are mixed.

Efficiency of a Heat Engine.—The efficiency of a heat engine may be measured by the proportion of the total heat absorbed at the higher temperature, which is converted into external work. Thus, if W represents the area ABCD, Fig. 153, then $\frac{W}{J}$ will represent the heat equivalent of the work performed by the gas during the direct cycle. Further,

$$\frac{W}{J} = Q_1 - Q_2,$$

by the First Law of Thermodynamics.

Therefore the efficiency ϵ of the engine, when absorbing heat at a temperature T_1, and discharging heat at a temperature T_2, may be written

$$\epsilon = \frac{\frac{W}{J}}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

Carnot's Theorem.—All reversible heat engines possess the same efficiency when absorbing and rejecting heat at the same two temperatures.—The truth of Carnot's theorem may be proved by showing that if it were false, the Second Law of Thermodynamics would be violated.

Let us suppose that we are provided with two heat engines, A and B, both of which, when working directly, absorb heat from a source maintained at a temperature T_1, and reject heat into a condenser maintained at a temperature T_2.

It is important to remark that no heat is supposed to be absorbed or rejected except at the two specified temperatures.

The working substances enclosed in the two cylinders may be different; we are in no way concerned with the form of the cylinders or with any mechanical details.

If the efficiencies of A and B are not equal, let us suppose that A has a greater efficiency than B. Then we may suppose that in B the length of stroke (*i.e.*, the distance through which the piston moves backwards or forwards) is so adjusted that the work performed in a complete cycle is equal to that performed by A under similar circumstances.

By means of suitable mechanism, A may be coupled so that when it works directly, it drives B reversely. Then, during each complete cycle, A will absorb a quantity Q_1 of heat at the temperature T_1, and reject a quantity Q_2 at a temperature T_2.

On the other hand, since B traverses the cycle in a reverse sense, it will absorb a quantity Q_2' of heat at a temperature T_2, and discharge a quantity Q_1' of heat at a temperature T_1.

Since equal amounts of work are performed in both cases, we have, in accordance with the First Law of Thermodynamics,

$$Q_1 - Q_2 = Q_1' - Q'_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1).$$

But if the efficiency of A is greater than that of B, we must have

$$\frac{Q_1 - Q_2}{Q_1} > \frac{Q_1' - Q_2'}{Q_1'} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2).$$

Therefore, dividing (2) by (1), we get $\frac{1}{Q_1} > \frac{1}{Q_1'}$.

$$\therefore Q_1' > Q_1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3).$$

Also $Q_2' > Q_2$, from (3) and (1).

This means that the quantity Q_1' of heat which B discharges into the source is greater than the quantity Q_1 which A absorbs from the source; whilst the quantity Q_2' of heat which B absorbs from the condenser is greater than the quantity Q_2 of heat which A discharges into the condenser. Hence during the performance of each complete cycle, a quantity of heat equal to

$$Q_1' - Q_1 = Q_2' - Q_2$$

will be transferred from the condenser at T_2 to the source at a higher temperature T_1. Since no external agency is supposed to aid the two engines, heat passes from a body at a low to one at a higher temperature without the performance of work by external agency. This is a violation of the Second Law of Thermodynamics.

Hence $Q_2' = Q_2$, and $Q_1' = Q_1$. Therefore $\frac{Q_1' - Q_2'}{Q_1'} = \frac{Q_1 - Q_2}{Q_1}$, and the efficiencies of the two engines are equal.

Remarks.—Some confusion is sometimes occasioned by the use of the word "engine" in the above argument. In ordinary language, the word engine is generally understood to refer almost exclusively to the mechanical arrangements used for facilitating the conversion of heat into work. In the general theory of heat engines as developed above, the term engine must be understood to apply almost exclusively to the working substance used in the conversion of heat into work. The mechanical arrangements used are in all cases supposed to be perfect, so far, at least, as is necessary in order that the theoretical conditions may be complied with.

The meaning of Carnot's theorem may be made clearer by the following illustrative example. Ether, water, and mercury, when heated (say) from 10° C. to 120° C., will all suffer changes of volume. In each case, too, the adiabatic elasticities will differ more or less from the isothermal elasticities. Let us suppose, then, that three engines are constructed so that

1. An isothermal expansion may take place at the temperature 120° C.
2. Adiabatic expansions and compressions may take place between 120° C. and 10° C.
3. An isothermal compression may be effected at the temperature 10° C.

Now during the expansions of the various substances the actual variations in volume, together with the forces called into play, will differ greatly. Further, different quantities of heat will be absorbed at T_1 and rejected at T_2. But in all three cases the ratio

$$\frac{\text{Work performed}}{\text{Heat absorbed from the source}}$$

will have the same value, provided no irreversible effects, such as those due to friction, are called into play.

Thus, ether might be used instead of steam as the working substance in an engine, without the theoretical efficiency of the engine being altered. In the case of mercury, the expansion would be very small, and the forces called into play would be correspondingly large. Hence a different mechanical construction would be necessary. But provided this were carried out so as to fulfil the theoretical conditions applying to a heat engine, liquid mercury could be successfully used as a working substance.

Actual heat engines will approximate to the theoretical efficiency of an ideal heat engine working between the prescribed temperatures, in proportion as the cycle traversed approximates to a reversible cycle; provided that heat is absorbed only at the higher temperature, and rejected only at the lower temperature. In no case can the efficiency of a heat engine be greater than that of an ideal heat engine working between the same temperatures.

In considering Carnot's cycle, it was assumed that a gas

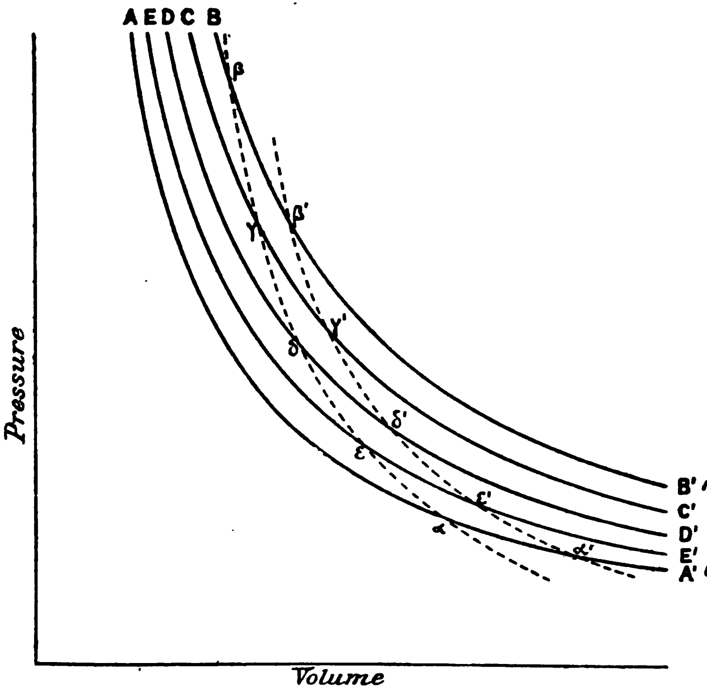

FIG. 154.—Graphic representation of Lord Kelvin's absolute scale of temperature.

was inclosed in the cylinder A (Fig. 151). We are now in a position to see that the value

$$\frac{Q_1 - Q_2}{Q_1}$$

will be the same, whatever working substance is inclosed in the cylinder. Thus, if internal work is performed in traversing the isothermals DA and BC (Fig. 153), the values of Q_1 and Q_2 will differ from the heat equivalents of the areas

DA*ad* and BC*cb*. Nevertheless $Q_1 - Q_2$ will be equal to the net amount of external work performed during the cycle, since the working substance is in the end brought back to its initial condition (p. 335). Also the efficiency

$$\frac{Q_1 - Q_2}{Q_1}$$

will be the same as for a perfect gas absorbing and rejecting heat at the same temperatures.

Lord Kelvin's Absolute Scale of Temperature.—Let us suppose that two isothermals have been obtained for a substance at two arbitrary but definite temperatures. Let these isothermals be represented by AA′ BB′, Fig. 154. For convenience we will suppose that the temperature corresponding to BB′ is that of water boiling under standard conditions (*see* Ch. II.), whilst the temperature corresponding to AA′ is that of melting ice.

Take any point β on BB′ and determine the adiabatic $\beta\alpha$, passing through this point; this adiabatic cuts the isothermal AA′ in the point α.

Now allow the substance to expand isothermally from the point β to β'; the amount of work performed may be measured in mechanical units. Next determine the adiabatic $\beta'\alpha'$, cutting the two isothermals in β' and α'. As previously explained, the external work performed by a reversible heat engine, whilst describing the cycle $\beta\beta'\alpha'\alpha$ between the temperatures of boiling water and melting ice, will be equal to the area $\beta\beta'\alpha'\alpha$.

Let us now divide the area $\beta\beta'\alpha'\alpha$ into any convenient number of equal parts by means of isothermal lines, such as CC′, DD′, EE′, &c. (Only four are shown in the figure, but the most convenient number would be 100). Then we have

$$\text{Area } \beta\beta'\gamma'\gamma = \text{area } \gamma\gamma'\delta'\delta = \text{area } \delta\delta'\epsilon'\epsilon = \text{area } \epsilon\epsilon'\alpha'\alpha.$$

Now let us define the temperature of any isothermal as proportional to the area enclosed by it and the two adiabatics $\beta\alpha$ and $\beta'\alpha'$, and the isothermal AA′. Thus, since the area $\epsilon\epsilon'\alpha'\alpha = \frac{1}{4}$ area $\beta\beta'\alpha'\alpha$, we may define the temperature corresponding to EE′ as $25° + \theta_0$, where θ_0 is the temperature corresponding to the isothermal AA′. The temperature corresponding to DD′ will be $50° + \theta_0$, and that corresponding to CC′ will be $75° + \theta_0$.

It may now be proved that *temperatures measured on this scale are independent of the nature of the substance, of which the isothermals and adiabatics have been used.*

For let the area $\beta\beta'a'a$ be equal to A, and let θ represent the temperature, measured on Lord Kelvin's scale, corresponding to any isothermal. Then the area enclosed by the isothermals for θ° and $(\theta - 1)^\circ$, and the adiabatics βa and $\beta' a'$, will be equal to $\frac{A}{100}$.

Now, this area will be equal to the difference between the heat Q_1 absorbed at θ, and the heat Q_2' rejected at $\theta - 1$, by a reversible engine working between these temperatures.

$$\therefore Q_1 - Q_2' = \frac{A}{100}.$$

Similarly, it follows that the area enclosed by two isothermals corresponding to the temperatures θ_1 and θ_2, and the two adiabatics βa and $\beta' a'$, will be equal to $(\theta_1 - \theta_2) \times \frac{A}{100}$. Also, if Q_2 is the heat rejected at θ_2 by a reversible engine working between θ_1 and θ_2, we have

$$Q_1 - Q_2 = (\theta_1 - \theta_2) \times \frac{A}{100} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

As a particular instance, let us suppose that the adiabatics βa and $\beta' a'$ are prolonged till they cut the isothermal corresponding to the condition of the substance when entirely deprived of heat. If a reversible engine be supposed to work between the temperature θ_1 and this latter temperature, no heat will be rejected from the engine at the lower temperature; all the heat will have been converted into work during the adiabatic expansion. Let us define the temperature of a substance when entirely deprived of heat as the absolute zero of temperature. Then in the above equation, if we measure temperatures from this zero, we shall have—

1. Since no heat is rejected at the lower temperature, $Q_2 = 0$.
2. Since the lower temperature is taken to be zero, $\theta_2 = 0$.

$$\therefore Q_1 - 0 = (\theta_1 - 0) \times \frac{A}{100}.$$

$$\therefore Q_1 = \theta_1 \times \frac{A}{100}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

In obtaining (2), we have substituted particular values for Q_2 and θ_2 in (1). But (1) is generally true for a heat engine absorbing a quantity of Q_1 of heat at θ_1, and rejecting a quantity Q_2 at θ_2, where θ_1 and θ_2 are any temperatures measured on Lord Kelvin's scale. Therefore, dividing the left hand side of (1) by Q_1, and the right hand side by the equal quantity $\theta_1 \times \frac{A}{100}$, we get the general relation

$$\frac{Q_1 - Q_2}{Q_1} = \frac{\theta_1 - \theta_2}{\theta_1}.$$

But $\frac{Q_1 - Q_2}{Q_1}$ is the efficiency of a heat engine working between the isothermals corresponding to θ_1 and θ_2. By Carnot's theorem, this is independent of the nature of the substance used to transform heat into work.

Therefore, $$\frac{\theta_1 - \theta_2}{\theta_1}$$

is independent of the nature of the substance used.

But $\frac{\theta_1 - \theta_2}{\theta_1} = 1 - \frac{\theta_2}{\theta_1}$. Hence, since 1 is a number and is therefore incapable of variations, the ratio $\frac{\theta_2}{\theta_1}$ of any two temperatures must be independent of the nature of the substance of which the isothermals and adiabatics have been used. That is, any substance of which the isothermals and adiabatics can be determined will serve equally well for measuring temperature, and the result obtained will be exactly the same whatever the substance may be.

Further, $$\frac{Q_1 - Q_2}{Q_1} = \frac{\theta_1 - \theta_2}{\theta_1} \quad \therefore\ 1 - \frac{Q_2}{Q_1} = 1 - \frac{\theta_2}{\theta_1}.$$

$$\therefore\ \frac{\theta_2}{\theta_1} = \frac{Q_2}{Q_1}$$

i.e., the ratio of any two temperatures is equal to the ratio of the heat absorbed to the heat rejected by an ideal heat engine working between those two temperatures.

It may also be noticed, that the value of a temperature measured in the above manner is independent of the particular adiabatics chosen.

Temperatures Measured on Lord Kelvin's Scale will agree with those Measured by the aid of a Perfect Gas Thermometer.—A perfect gas conforms to the conditions prescribed in the dynamical theory of gases. Hence we have the equation

$$pv = RT = \tfrac{1}{3} MV^2 \text{ (p. 293)}$$

where T is measured by the constant pressure gas thermometer.

When T=0, V=0, *i.e.*, the molecules of the gas will be reduced to complete quiescence, and will therefore be entirely deprived of energy, which we have learnt to consider as equivalent to heat. Hence at the absolute zero, as measured by the perfect gas thermometer, the condition of a substance will be the same as at the absolute zero measured on Lord Kelvin's scale.

Also there are 100° between the melting point of ice and the boiling point of water, on both scales.

It remains to be proved that the magnitude of a degree is the same on both scales. We will do this by determining the work performed in traversing a Carnot's cycle, heat being absorbed at a temperature T_1, and rejected at a temperature T_2, T_1 and T_2 *being measured by the perfect gas thermometer.*

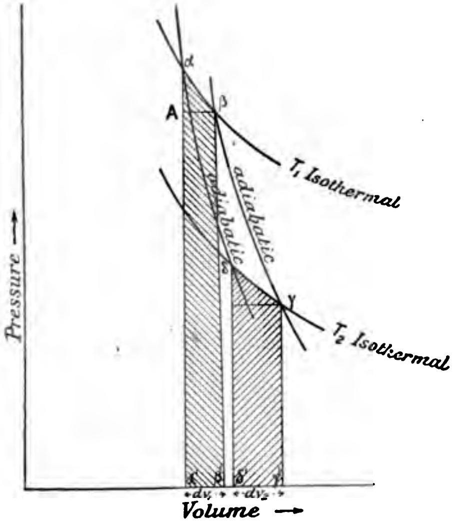

FIG. 155.—Heat absorbed and rejected by a perfect gas when traversing a Carnot's Cycle.

Let us suppose that $\alpha\beta$, $\delta\gamma$, Fig. 155, are parts of isothermals of a perfect gas when at the respective temperatures T_1 and T_2 (measured from −273°C.) respectively.

Let α represent the initial condition of the gas. Allow it to expand isothermally through a small increment of volume dv_1, the point β thus being reached. Now the pressure at α will be greater than that at β; but if dv_1 is very small, *i.e.*, if α and β are very close together, we may assume that the work performed during the above expansion is equal to the pressure at β multiplied by the increase of volume, between a and β, *i.e.*, work performed = area $A\beta\beta'a'$, Fig. 155. We have thus neglected the area of the small triangle $a\beta A$, which is seen to be small in comparison with the area $A\beta\beta'a'$.

Let $p_1 = \beta\beta' =$ the pressure at β.

The work performed in passing from a to $\beta = p_1 dv_1$ (p. 297).

In a perfect gas no internal work is performed during expansion, *i.e.*, no work is performed in separating the molecules from each other. Therefore the only heat absorbed during the expansion will be that corresponding to the external work $p_1 dv_1$ performed.

∴ Quantity of heat Q_1, absorbed at temperature T_1

$$= \frac{p_1 dv_1}{J}. \quad \text{(First Law of Thermodynamics.)}$$

Allow the gas to expand adiabatically till the temperature T_2 is reached. The adiabatic $\beta\gamma$ will be traversed from β to γ Let p_2 and v_2 be the pressure and volume corresponding to the point γ.

Now compress the gas isothermally till a point δ on the adiabatic passing through a is reached. If the decrease in volume so produced is equal to dv_2, it may be shown by reasoning similar to that already employed, that the work performed on the gas is equal to $p_2 dv_2$.

∴ Quantity of heat Q_2, rejected at the temperature T_2

$$= \frac{p_2 dv_2}{J}. \quad \text{(First Law of Thermodynamics.)}$$

We may now compress the gas adiabatically from δ to a, when it will have attained its initial condition.

Hence the efficiency of an ideal heat engine working between T_1 and T_2

$$= \epsilon = \frac{Q_1 - Q_2}{Q_1} = \frac{\frac{p_1 dv_1}{J} - \frac{p_2 dv_2}{J}}{\frac{p_1 dv_1}{J}} = \frac{p_1 dv_1 - p_2 dv_2}{p_1 dv_1}.$$

It now remains for us to determine the value of the members on the right hand side of this equation in terms of T_1 and T_2.

Since β is on the isothermal for $T_1°$, we have

$$p_1v_1 = RT_1.$$

$$\therefore p_1 = \frac{RT_1}{v_1}.$$

$$\therefore p_1dv_1 = RT_1\frac{dv_1}{v_1}.$$

Since the point γ is on the isothermal for $T_2°$, we have

$$p_2v_2 = RT_2.$$

$$\therefore p_2 = \frac{RT_2}{v_2}.$$

$$p_2dv_2 = RT_2\frac{dv_2}{v_2}.$$

$$\therefore e = \frac{Q_1 - Q_2}{Q_1} = \frac{RT_1\frac{dv_1}{v_1} - RT_2\frac{dv_2}{v_2}}{RT_1\frac{dv_1}{v_1}} = \frac{T_1\frac{dv_1}{v_1} - T_2\frac{dv_2}{v_2}}{T_1\frac{dv_1}{v_1}} \quad (1).$$

The values of the ratios $\frac{dv_1}{v_1}$ and $\frac{dv_2}{v_2}$ may be determined from the condition that β and γ are on one adiabatic, whilst α and δ are on another adiabatic.

First, let us determine the ratio $\frac{v_1}{v_2}$ of the volumes occupied by the gas at β and γ respectively.

Since β and γ are on an adiabatic

$$p_1v_1^{\gamma} = p_2v_2^{\gamma}.$$

$$\therefore \left(\frac{v_1}{v_2}\right)^{\gamma} = \frac{p_2}{p_1} \quad \ldots\ldots\ldots \quad (2).$$

But

$$p_1 = \frac{RT_1}{v_1}$$

$$\text{and } p_2 = \frac{RT_2}{v_2}.$$

Substituting these values for p_1 and p_2 in the right hand member of (2), we get

$$\left(\frac{v_1}{v_2}\right)^{\gamma} = \frac{RT_2}{v_2} \div \frac{RT_1}{v_1} = \frac{v_1}{v_2} \cdot \frac{T_2}{T_1}.$$

Dividing both sides of this equation by $\left(\frac{v_1}{v_2}\right)$ we get

$$\left(\frac{v_1}{v_2}\right)^{\gamma - 1} = \frac{T_2}{T_1}.$$

$$\therefore \frac{v_1}{v_2} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma - 1}}$$

Now this value for the ratio of the volumes occupied by gas at β and

γ is independent of the pressures, and therefore of the particular adiabatic on which the points may be situated. Therefore we must have

$$\frac{\text{Volume occupied by gas at } a}{\text{Volume occupied by gas at } \delta} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma - 1}}$$

$$\therefore \frac{v_1 - dv_1}{v_2 - dv_2} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma - 1}} = \frac{v_1}{v_2}.$$

Therefore, multiplying across, we get

$$v_2(v_1 - dv_1) = v_1(v_2 - dv_2).$$
$$v_1v_2 - v_2dv_1 = v_1v_2 - v_1dv_2.$$
$$\therefore v_2dv_1 = v_1dv_2.$$
$$\frac{dv_1}{v_1} = \frac{dv_2}{v_2}.$$

Substituting this value of $\frac{dv_1}{v_1}$ in (1), we get

$$\epsilon = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1\frac{dv_2}{v_2} - T_2\frac{dv_2}{v_2}}{T_1\frac{dv_2}{v_2}} = \frac{T_1 - T_2}{T_1}.$$

But we have seen that on Lord Kelvin's thermodynamic scale of temperature

$$\frac{Q_1 - Q_2}{Q_1} = \frac{\theta_1 - \theta_2}{\theta_1}.$$

If θ_1 is the absolute temperature of boiling water, θ_2 being that of melting ice, then $\theta_1 - \theta_2 = 100$. On the perfect gas thermometer we should similarly have $T_1 - T_2 = 100$, for the same difference of temperature.

$\therefore \epsilon = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} = \frac{100}{T_1}$, using the perfect gas thermometer.

$\epsilon = \frac{Q_1 - Q_2}{Q_1} = \frac{\theta_1 - \theta_2}{\theta_1} = \frac{100}{\theta_1}$, using Lord Kelvin's scale of temperature.

Since ϵ must have the same value in both cases, we have

$$\frac{100}{T_1} = \frac{100}{\theta_1}.$$
$$\therefore T_1 = \theta_1,$$

i.e., the absolute temperature of boiling water is the same whether measured by the perfect gas thermometer or on Lord Kelvin's absolute scale of temperature.

In the same way, it may be shown that any other temperature will have the same value on the two scales.

Advantages of Lord Kelvin's Absolute Scale of Temperature.—In measuring temperatures by the expansion of some substance, the magnitude of a degree will depend more or less on the nature of the substance. Even with a gas thermometer the magnitude of a degree will vary according as carbon-dioxide or hydrogen is used.

The ultimate aim of science is to obtain all measurements in terms of the fundamental units of length, mass, and time, or in terms of a derived unit, such, for instance, as that of energy.

But in utilising the expansion of a substance in measuring temperature, a property of a particular substance is involved.

On the other hand, when θ_1 and θ_2 are measured on Lord Kelvin's scale, we have :—

$$\frac{\theta_1}{\theta_2} = \frac{Q_1}{Q_2}.$$

Q_1 and Q_2 can be measured in terms of energy, since by the first law of thermodynamics, heat is proportional to work. Therefore, the ratio of any two temperatures may be obtained from purely mechanical considerations, and will be independent of the particular substance used in the conversion of work into heat.

Lord Kelvin's thermodynamic scale of temperature is therefore *absolute* in the true sense of the term.

The magnitude of θ_1 and θ_2 will depend on the fixed points chosen. It is most convenient to choose these as the boiling point of water and the melting point of ice.

Supposing that we could obtain a quantity of a *perfect gas, i.e.*, a gas which would obey Boyle's law for all pressures, then the ratio of any two temperatures, as measured by the expansion of this gas at constant pressure, would be equal to the ratio of the corresponding temperatures measured on Lord Kelvin's scale. If the same fixed points were chosen in both cases, then the absolute magnitude of a temperature would be the same, whichever of these two systems was used.

Now experiment has shown that no gas can be considered "perfect," in the above sense of the term. The product of the pressure and volume of hydrogen remains most nearly constant (p. 203), whilst the other "permanent" gases exhibit greater deviations from Boyle's law. Temperatures measured on the constant pressure hydrogen thermometer will coincide, to a close approximation, with those measured on Lord Kelvin's absolute scale.

Entropy.—In passing along an adiabatic, such as $\alpha\epsilon\delta\gamma\beta$, Fig. 154, successive changes of temperature are experienced by a substance. At β the temperature of the substance will be that of water boiling under standard conditions, whilst at α the temperature will be that of melting ice; all intermediate temperatures will be successively attained in passing from α to β.

Moreover, in passing from one isothermal to another, the same alteration in temperature will be experienced, no matter what adiabatic is traversed. This is self-evident, since by definition a substance has the same temperature at all points on an isothermal. Hence since γ and γ' are on the isothermal CC′, these points will correspond to equal temperatures. Similarly β and β' will correspond to equal temperatures. Therefore, in passing from γ to β, the rise in temperature will be equal to that on passing from γ' to β'.

Let us now turn our attention to the thermal changes which correspond to the passage, along an isothermal, from one adiabatic to another. During this transformation, the temperature remains constant, and a certain quantity of heat enters the body *if external work is performed by it, or if its internal energy is increased,* or is rejected by the body *if work is performed on it by external agency, or if its internal energy is diminished.*

Now during the passage along different isothermals, equal quantities of heat will not be absorbed or rejected between the same adiabatics. Thus, from Carnot's theorem, if Q_1 units of heat are absorbed in passing from β to β', Fig. 154, at the constant temperature θ_1, then Q_2 units will be given up during the passage from γ' to γ at the temperature θ_2; the relations between Q_1 and Q_2 being expressed by the equations :—

$$Q_1 - Q_2 = \text{area } \beta\beta'\gamma'\gamma.$$

$$\frac{Q_1 - Q_2}{Q_1} = \frac{\theta_1 - \theta_2}{\theta_1}.$$

$$\therefore \frac{Q_2}{Q_1} = \frac{\theta_2}{\theta_1} \text{ (\textit{see} p. 347)}.$$

$$\therefore \frac{Q_2}{\theta_2} = \frac{Q_1}{\theta_1}.$$

Further, the above operations are *reversible*, *i.e.*, if Q_2 units of heat are *given up* during a compression from γ' to γ at a temperature θ_2, Q_2 units will be *absorbed* during an expansion from γ to γ'.

In the same way it may be shown that in passing along the isothermal for θ_3 from any point δ on the adiabatic $\beta\gamma\delta\alpha$ to a point δ' on the adiabatic $\beta'\gamma'\delta'\alpha'$, the amount of heat Q_3 absorbed will be given by the relation

$$\frac{Q_3}{\theta_3} = \frac{Q_2}{\theta_2} = \frac{Q_1}{\theta_1}.$$

Hence in passing along any isothermal from one adiabatic to another, the ratio

$$\frac{\text{Heat absorbed (or rejected)}}{\text{Absolute temperature corresponding to isothermal traversed}}$$

will be constant, whatever isothermal path is chosen.

This ratio may be used to distinguish different adiabatics, just as different isothermals are distinguished by their temperatures.

Let us take any adiabatic $\beta\gamma\delta\epsilon\alpha$ as a standard, and draw the adiabatic $\beta'\gamma'\delta'\epsilon'\alpha'$, so that

$$\frac{Q_1}{\theta_1} = \frac{Q_2}{\theta_2} = \frac{Q_3}{\theta_3} = 1.$$

We might then draw another adiabatic in such a position that the ratio,

$$\frac{\text{Heat absorbed during the passage to it from } \beta'\gamma'\delta'\epsilon'\alpha' :}{\text{Temperature corresponding to the isotherma path chosen,}}$$

should be 1.

Proceeding in this way we might divide the whole of the diagram up by consecutive adiabatics, distinguished by the characteristic that in passing isothermally from one to another

$$\frac{\text{Heat absorbed (or rejected)}}{\text{Absolute temperature corresponding to isothermal traversed}} = 1.$$

This characteristic property distinguishing one adiabatic from another is termed *difference of entropy*.

Since all points on an adiabatic will be characterised by the same entropy, we may define this quantity as follows :—

The term Entropy is applied to that thermal property of a substance which remains constant as long as heat is not communicated to or abstracted from it by external bodies.

Adiabatics are sometimes termed isentropics (*i.e.*, lines of equal entropy). When heat enters a substance, its entropy increases. The increase in entropy is measured by

$$\frac{Q}{\theta}$$

where Q is the heat absorbed, and θ is the absolute temperature during the absorption.

Method of Measuring Entropy.—Let us define the condition corresponding to zero entropy by the intersection of a particular adiabatic with a certain isothermal. Let A be the point so obtained. It will correspond to a definite temperature θ and pressure p.

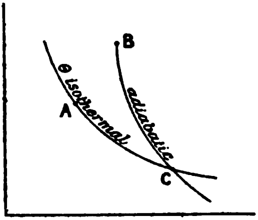

FIG. 156.—Method of measuring entropy.

Let B represent the condition of one gram of a substance, and let it be required to determine the entropy corresponding to this point.

Allow the substance to expand adiabatically till its temperature sinks to θ, the standard temperature. No change of entropy will occur during this transformation. Hence, the entropy of the substance at C will be equal to that at B.

Now compress the substance isothermally till the point A is reached. Let Q units of heat be rejected during this process. Then the difference in entropy between C and A is equal to

$$\frac{Q}{\theta}.$$

Hence, we may say that the entropy of the substance at B is equal to

$$\frac{Q}{\theta}.$$

The Entropy of any System always tends to increase to a Maximum Value.—The truth of this proposition, due to Clausius, may easily be seen if we remember that heat always tends to pass from bodies at high to those at lower temperatures.

When bodies at different temperatures are put in thermal communication, the fact that the temperatures tend to become equalised led to our first idea of heat as a quantity

(p. 111). We there assumed that heat was something which passed from the warm to the colder body, during the equalisation of temperature. In the case of a self-acting heat engine, heat is always absorbed at a high and rejected at a lower temperature (p. 339).

Let us suppose that a quantity Q of heat flows from a warm body at a temperature θ_1 to a colder body at a temperature θ_2.

The loss of entropy of warm body $= \dfrac{Q}{\theta_1}$.

Gain of entropy of colder body $= \dfrac{Q}{\theta_2}$.

$\therefore$ Gain of entropy of the system comprising both bodies =

$$\frac{Q}{\theta_2} - \frac{Q}{\theta_1} = Q\,\frac{\theta_1 - \theta_2}{\theta_1\theta_2}.$$

Since θ_1 is greater then θ_2, $\theta_1 - \theta_2$ is positive. Therefore, the entropy of the system is increased by the passage of heat from the body at θ_1 to the colder body at θ_2.

To express the external work performed in traversing a Carnot's cycle in terms of differences of temperature and of entropy.

Let Q_1 units of heat be absorbed at the temperature θ_1.

Let Q_2 units of heat be rejected at the temperature θ_2.

According to the first law of thermodynamics, work performed in traversing the cycle = area of cycle = $J\ (Q_1 - Q_2)$, if Q_1 and Q_2 are measured in therms.

During the absorption of Q_1 units of heat at a temperature θ_1, the entropy will be increased by $\dfrac{Q_1}{\theta_1}$.

Let us suppose that the entropies corresponding to the two adiabatics forming part of the cycle are ϕ_1 and ϕ_2.

Then

$$\frac{Q_1}{\theta_1} = \phi_2 - \phi_1. \quad \therefore\ Q_1 = \theta_1\,(\phi_2 - \phi_1).$$

Similarly, since the heat Q_2 is absorbed at the temperature θ_2, in passing between the same two adiabatics

$$\frac{Q_2}{\theta_2} = \phi_2 - \phi_1. \quad \therefore\ Q_2 = \theta_2\,(\phi_2 - \phi_1).$$

$$\therefore\ Q_1 - Q_2 = (\theta_1 - \theta_2)\,(\phi_2 - \phi_1).$$

$\therefore$ Work performed during cycle $= J(Q_1 - Q_2) = J(\theta_1 - \theta_2)(\phi_2 - \phi_1)$.

Temperature-Entropy Diagrams.—In defining the condition of a substance, instead of specifying its pressure, volume, and temperature, it is often preferable to state its temperature and entropy.

We may mark off equal increments of entropy along a horizontal axis, and equal increments of temperature along the vertical axis.

The isothermals will be straight lines parallel to the axis of entropy, and the isentropics (p. 355) will be straight lines parallel to the axis of temperature.

In order to fix our ideas, let us represent a Carnot's cycle by means of a temperature-entropy diagram.

Let us suppose that 2,900 units of heat (measured in therms.) are absorbed at the temperature θ_1, say 290° (absolute).

During this process, the entropy is increased by $\phi_2 - \phi_1 = \frac{2{,}900}{290} = 10$ units. Take any point A, Fig. 157, on the 290° isothermal, and mark off to the right of this a distance equal to the 10 units on the entropy scale. We thus obtain the line AB, representing the isothermal expansion at the higher temperature.

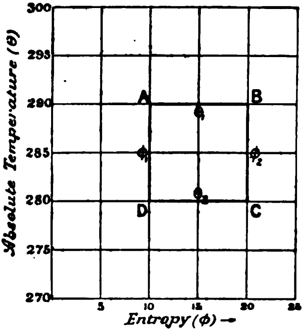

FIG. 157.—Entropy-temperature diagram of a Carnot's cycle.

During the adiabatic expansion, the entropy remains constant, whilst the temperature falls. Hence this operation will be represented by a straight line parallel to the axis of temperature.

Let the temperature of the condenser be 280°. Then the line BC will represent the adiabatic expansion.

Now during the isothermal compression of the substance at the lower temperature, the entropy is decreased by an amount equal to the increase of entropy during the expansion at the higher temperature. This follows from the relation

$$\frac{Q_1}{\theta_1} = \frac{Q_2}{\theta_2} = \phi_2 - \phi_1.$$

Therefore CD represents the compression at the temperature θ_2 (280° absolute).

It can easily be seen that DA represents the final adiabatic compression, by which the substance is brought back to its initial condition A.

Work performed during the above cycle $= J(\theta_1 - \theta_2)(\phi_2 - \phi_1)$ $= J \times AD \times AB = J \times$ area of the square ABC $= 100$ J ergs.

The fact that an ideal heat engine describing a simple cycle, has a maximum efficiency for an engine working between the given temperatures, may be instructively illustrated by the aid of a $\theta\phi$ diagram.

Heat absorbed at upper temperature $\theta_1 = Q_1 = \theta_1(\phi_2 - \phi_1)$.

∴ Efficiency of any ideal heat engine describing a simple cycle

$$= \frac{Q_1 - Q_2}{Q_1} = \frac{\theta_1 - \theta_2}{\theta_1}.$$

For the cycle ABCD, Fig. 158,

$$= \frac{Q_1 - Q_2}{Q_1} = \frac{10}{290} = \cdot 0345.$$

Now let us draw any other figure such as ABECDFA.

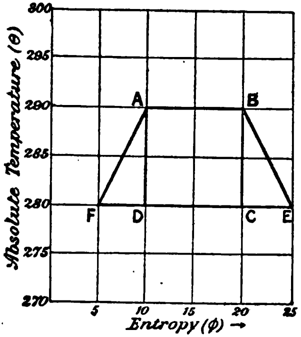

FIG. 158.—$\theta\phi$ diagram of simple cycle, and cycle in which heat is absorbed at various temperatures.

In this case the work performed during a cycle = J × area ABEF. The heat absorbed at the temperature $\theta_1 = \theta_1 \times AB$ = 2,900 therms., as before. But in passing along BE, the entropy has been increased by five units. Hence heat was being continually absorbed whilst the path BE was being traversed.

Now the average temperature along the path BE = 285° (absolute).

∴ Total heat absorbed in passing from B to E = average temperature × difference of entropy between E and B = 285 × 5 = 1,425 therms.

In passing E to F, a quantity of heat, equal to $\theta_2 \times FE = 280 \times 20 = 5{,}600$ therms, is rejected.

In passing from F to A, a quantity of heat, equal to the average temperature along FA × difference in entropy between A and F = 285 × 5 = 1,425 therms, is absorbed.

$\therefore$ Total heat absorbed = 2,900 + 2 × 1,425 = 2,900 + 2,850 = 5,750 therms.

Work performed during cycle = J × (heat absorbed − heat rejected) = J × (5,750 − 5,600) = 150 J ergs.

$\therefore$ Efficiency of engine describing the cycle ABEFA $= \frac{150}{5{,}750} = \cdot026$.

Therefore the efficiency of a heat engine is diminished if part of the heat absorbed is taken in at temperatures intermediate between those of the source and of the condenser.

To construct a $\theta\phi$ Diagram for 1 gram of Water and Saturated Steam.—When a gram of water is heated from 0° C. to 1° C., 1 therm of heat is communicated to it, and the absolute temperature is changed from 273° to 274°. The average absolute temperature during this operation is 273·5°; therefore, it follows that, to a first approximation, the entropy of the gram of water is increased by $\frac{1}{273\cdot5}$, whilst it is being heated from 0° C. to 1° C.

For convenience, the zero of entropy is generally taken to correspond to water at 0° C. Hence, the entropy of 1 gram of water at 1° C. $= \frac{1}{273\cdot5} = \cdot003656$.

Neglecting the variation in the specific heat of water (*see* p. 134), it follows that when a gram of water is heated from 10° C. to 11° C. (283° to 284°, on the absolute scale) the entropy is increased by $\frac{1}{283\cdot5} = \cdot003527$.

Proceeding in this manner we can construct a table similar to that given on the next page.

(It is of course supposed that the water remains in the liquid condition throughout the above operations. For temperatures higher than 100° C., ebullition is supposed to be prevented by the application of a sufficiently high pressure.)

APPROXIMATE INCREASE IN THE ENTROPY OF ONE GRAM OF WATER, FOR A RISE OF TEMPERATURE OF 1° C.

Temperature of Water.	Increase of Entropy per degree.	Temperature of Water.	Increase of Entropy per degree.
0° C.	·003656	110° C.	·002607
10	·003527	120	·002542
20	·003407	130	·002478
30	·003296	140	·002418
40	·003190	150	·002361
50	·003091	160	·002307
60	·002999	170	·002255
70	·002912	180	·002205
80	·002829	190	·002157
90	·002751	200	·002112
100	·002677	210	·002068

To find the entropy of a gram of water at any temperature (say 50° C.), we proceed as follows—

Add together the numbers in the second column opposite the temperatures 0°, 10°, 20°, ... 50°.

Divide the number so obtained by six, in order to get the average increase in the entropy of 1 gram of water, between 0° C. and 50° C., for a rise of 1° C.

We thus find

Average increase in entropy per degree Centigrade between 0° and 50° = ·003361.

∴ Increase in entropy for a rise in temperature of 50° = 50 × ·003661 = ·1680.

∴ Entropy of 1 gram of water at 50° = ·1680.

In a similar manner, calculate the entropy of 1 gram of water at 25°, 50°, 75°, 100°, 125°, 150°, 175°, 200°, and plot these values or a $\theta\phi$ diagram similar to Fig. 159. The curve obtained by joining these points is termed the *water line*.

The entropy ϕ of 1 gram of water, at an absolute temperature T, can also be calculated from the formula

$$\phi = 2{\cdot}30\{\log_{10} T - \log_{10} 273\}.$$

In order to obtain the steam line, it is only necessary to remember that in order to convert 1 gram of water at any temperature into saturated steam at the same temperature, a certain amount of heat, termed the latent heat of vaporisation, must be communicated to the water. Let L_t be the latent heat of steam, at a temperature *t*. This varies with the temperature of vaporisation (*see* p. 155). Then since the temperature is not changed by the communication of this heat, the increase of entropy $= \dfrac{L_t}{273 + t}$.

The value of L_t may be calculated from Regnault's formula (*see* p. 155), or obtained from the following table:—

PROPERTIES OF SATURATED STEAM.

Temp. C.	Latent Heat (L_t).	Pressure in mm. of mercury.	Specific volume in litres per gram.	Temp. C.	Latent Heat (L_t).	Pressure in mm. of mercury.	Specific volume in litres per gram.
0°	606·5	4·60	210·66	100	536·5	760·00	1·6496
5	603·0	6·53	150·23	105	533·0	906·41	1·3978
10	599·5	9·17	108·51	110	529·4	1075·4	1·1903
15	596·0	12·70	79·35	115	525·8	1269·4	1·0184
20	592·6	17·39	78·72	120	522·3	1491·3	0·8752
25	589·1	23·55	43·96	125	518·7	1743·9	0·7555
30	585·6	31·55	33·27	130	515·1	2030·3	0·6548
35	582·1	41·83	25·44	135	511·6	2353·7	0·5698
40	587·6	54·91	19·64	140	508·0	2717·6	0·4977
45	575·1	71·39	15·31	145	504·4	3125·6	0·4363
50	571·7	91·98	12·049	150	500·8	3581·2	0·3839
55	568·2	117·47	9·501	155	497·2	4088·6	0·3388
60	564·7	148·79	7·653	160	493·5	4651·6	0·3001
65	561·1	186·94	6·171	165	489·9	5274·5	0·2665
70	557·6	233·08	5·014	170	486·3	5961·7	0·2375
75	554·1	288·50	4·102	175	482·7	6717·4	0·2122
80	550·6	354·62	3·379	180	479·0	7546·4	0·1901
85	547·1	433·00	2·800	185	475·3	8453·2	0·1708
90	543·6	525·39	2·334	190	471·7	9442·7	0·1538
95	540·0	633·69	1·957	195	468·0	10,520	0·1389
				200	464·3	11,689	0·1257

For example, in order to vaporise 1 gram of water at 50° without raising its temperature, 571·7 therms must be communicated to it. The absolute temperature throughout the operation is 273 + 50 = 323. Therefore the increase of entropy

$$= \frac{571\cdot7}{323} = 1\cdot77.$$

Now, the entropy of 1 gram of water at 50° = ·168. Therefore the entropy of 1 gram of saturated steam at 50° = 1·77 + ·168 = 1·938.

In a similar manner, with the aid of the above table, calculate the entropy of 1 gram of saturated steam at 25°, 50°, 75°, . . .

200°. Plot these values on the $\theta\phi$ diagram. The curve joining the points so obtained is termed the *steam line.*

It will be sufficiently obvious from the above reasoning that

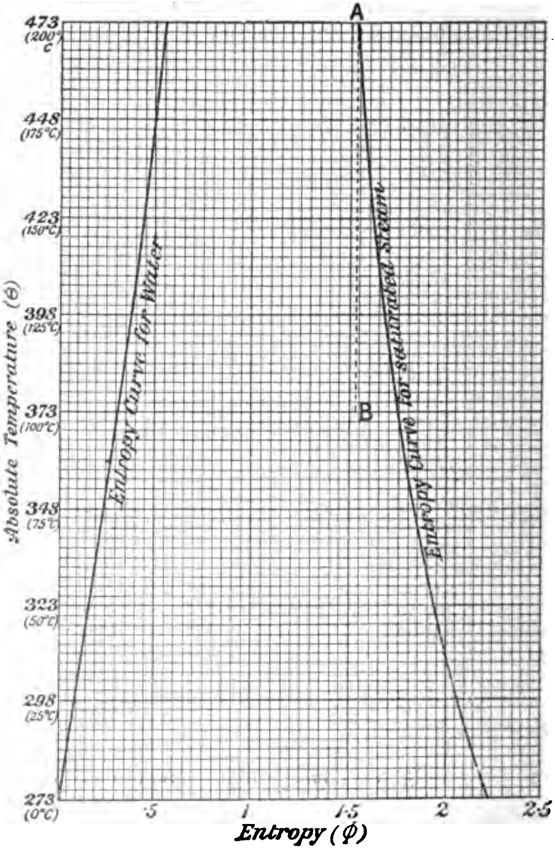

FIG. 159.—$\theta\phi$ diagram for water and saturated steam.

the entropy of 2 grams of a substance at any temperature will be twice as great as the entropy of 1 gram of the substance at the same temperature.

Further, during the vaporisation of 1 gram of water, all points on the horizontal line in Fig. 159 passing through the temperature at which the vaporisation occurs, will be successively attained. Thus when half the water is vaporised, a point midway between the water and steam lines will be reached. Generally, if the distance between the water and steam lines at any temperature is d, and if the entropy of 1 gram of a mixture of water and saturated steam at the same temperature, is represented by a point at a distance x from the steam line, then $\frac{x}{d}$ grams of the water will be in the liquid condition, and $\frac{d-x}{d}$ grams will have been converted into saturated steam.

Problem.—Show that if 1 gram of saturated steam at a temperature 200° C. is allowed to expand adiabatically, performing external work till its temperature falls to 100° C., then part of the steam will be condensed. Also, find the mass of water thus formed. (Compare with Hirn's experiment, p. 331.)

An adiabatic, as already explained, is represented by a vertical straight line on the $\theta\phi$ diagram. The point A (Fig. 159) corresponds to 1 gram of saturated steam at 200°. Draw the line AB parallel to the axis of temperatures. Then AB is an adiabatic or isentropic line. The point B on this line, corresponding to a temperature of 100° C., is seen to be situated between the steam and water lines, and therefore, as already explained, corresponds to a mixture of water and saturated steam.

Also, horizontal distance from B to steam line $= x = \cdot 22$ entropy scale divisions.

Horizontal distance between water line and steam line at 100° $= d = 1\cdot 44$ entropy scale divisions.

$$\therefore \text{ Steam condensed} = \frac{\cdot 22}{1\cdot 44} = \cdot 15 \text{ grams.}$$

If the above problem had been given in terms of saturated steam at certain pressures, the corresponding temperatures could have been obtained from the table on p. 361, and the above procedure followed.

Dissipation and Degradation of Energy.—The first law of thermodynamics is a particular application of the more general law of the **Conservation of Energy.** According to this latter law, the total amount of energy in the universe remains constant, whatever changes may take place in its distribution. The first law of thermodynamics simply states that if mechanical energy is transformed into heat, the mechanical energy used up is equivalent to the heat produced. Or, in the converse case, where heat is used up in performing work, the heat which disappears is equivalent to the work performed.

On the other hand, the second law of thermodynamics states that work can only be performed by a heat engine when heat passes from a body at a high, to another at a lower temperature.

Hence the conversion of heat into mechanical work must always tend to lower the temperature of the source, and raise the temperature of the condenser of an engine.

If the universe were at a constant temperature throughout, its heat could not by any known process be converted into work. For this latter purpose, we must have a source of heat at a high temperature and a condenser at a lower temperature.

Now all the activities at work throughout the universe tend to the final equalisation of temperature. Hence these activities tend to bring about a state of things in which further conversion of heat into work will be impossible.

The result of this is, that though the amount of energy in the universe cannot increase or decrease, that proportion of this energy which can be used for mechanical purposes is continually decreasing.

This may also be seen if we consider the case of two large reservoirs of water at different levels. Water may be allowed to flow from the reservoir at the higher to that at the lower level, and work may be performed if we constrain this water to drive turbines or mill-wheels. But the difference in level of the surfaces of the water in the two reservoirs will continually diminish, so that a state will finally be reached in which no further work can be obtained from the system.

Intrinsic Energy.—Let us suppose the condition of a substance is represented by the point A, Fig. 160. If this substance were enclosed in a vessel the walls of which are perfect non-conductors of heat, and if the volume of the vessel could be indefinitely increased, then by suitably varying the external pressure, the substance could be permitted to expand adiabatically along the curve ABC, till the absolute zero isothermal was reached. The external work performed in the expansion would be equal to the area bounded by the line AD, together with the curve ABC and the line DE, produced till they meet.

But at the absolute zero, the substance would possess no heat, and therefore no energy. All of the energy possessed by the substance at A would have been converted into work during the expansion. Therefore the area bound by AD together with the curve ABC and the line DE produced till they meet, represents the work which could be performed by the substance without receiving energy from without. Hence the area ABC .... EDA is said to be equal to the intrinsic energy of the substance. In the case of a perfect gas, it may be shown that the intrinsic energy is independent of the pressure of the gas.

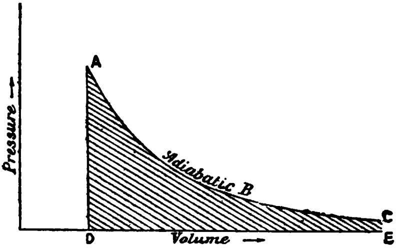

FIG. 160.—Graphic representation of the intrinsic energy of a substance.

SUMMARY TO CHAPTER XVI.

Cyclical Operations.—When, after any changes have been produced in a substance, that substance is brought back to its initial condition, a cycle of operations is said to have been performed.

Reversible Cycles.—If a substance can be caused to traverse a cycle in opposite directions, and the thermal actions at all points are reversed when the direction of traversing the cycle is reversed, the cycle is said to be reversible. In a reversible cycle, if heat is generated in traversing one part of the cycle in one direction, an equal quantity of heat must be absorbed in traversing that part of the cycle in a reverse direction.

Friction renders a cycle irreversible, since heat is produced by friction in whichever direction the cycle is traversed.

A simple cycle consists of two isothermal and two adiabatic transformations. When heat is absorbed at the higher temperature, and rejected at the lower temperature, the cycle is traversed in the direction in which the hands of a clock revolve, and a net amount of external work, equal to the area of the cycle (if pressures and volumes are measured in dynes and c.cs. respectively) is performed. This is said to be a **direct cycle.**

In **a reversed cycle** heat is absorbed at the lower, and given out at the higher temperature. The cycle is then traversed in a direction opposite to that in which the hands of a clock revolve, and an amount of work equal to the area of the cycle must be performed by external agency.

In both direct and reversed cycles the work performed is equal to the difference between the heat absorbed and that given out. This follows from the first law of thermodynamics.

The Second Law of Thermodynamics.—"*It is impossible for a self-acting machine, unaided by any external agency, to convey heat from a body at a low to one at a higher temperature; or heat cannot of itself (i.e., without the performance of work by some external agency) pass from a cold to a warmer body.*"—Clausius.

"*It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of surrounding objects.*"—(Lord Kelvin.)

In Clausius's form of the second law, attention is directed to the conditions necessary for the transference of heat from one body to another.

In Lord Kelvin's form of the second law, attention is directed to the conditions necessary for the transformation of heat into work. Both forms of the second law are, however, equivalent.

It must be particularly remembered that the second law of thermodynamics applies only to cyclical operations.

The efficiency of a heat engine is equal to the proportion of the total heat absorbed at the higher temperature, which is converted into external work whilst a direct cycle is being traversed.

Carnot's Theorem.—*All reversible heat engines possess the same efficiency when absorbing and rejecting heat at the same two temperatures.*

Lord Kelvin's Absolute Scale of Temperature.—Two isothermals corresponding to arbitrary but definite temperatures having been obtained, two adiabatics are drawn, so that a portion of the *p.v.* diagram is completely inclosed. The inclosed area is divided into a convenient number of equal elements of area by means of isothermal lines.

Temperatures corresponding to these isothermals are then numbered consecutively.

The efficiency of a reversible heat engine absorbing a quantity Q_1 of heat at a temperature θ_1, and rejecting a quantity Q_2 of heat at a temperature θ_2, is expressed by the relation

$$\frac{Q_1 - Q_2}{Q_1} = \frac{\theta_1 - \theta_2}{\theta_1} = \frac{T_1 - T_2}{T_1},$$

where T_1 and T_2 denote the temperatures, measured on the perfect gas thermometer, which correspond to θ_1 and θ_2 on Lord Kelvin's scale.

Entropy.—In passing along an isothermal from one adiabatic to another, a certain amount of heat is absorbed or rejected. If the value of this quantity of heat is divided by the absolute temperature corresponding to the isothermal traversed, the result will be the same whatever isothermal is chosen, and is termed change of **entropy.** This gives us a convenient method of distinguishing between different adiabatics, just as different isothermals are distinguished by their temperatures.

QUESTIONS ON CHAPTER XVI.

(1) A cylinder of compressed air bursts. The gas is cooled below the coldest ot surrounding objects, and external work is done. How do you reconcile these facts with the axiom on which the second law of thermodynamics is based?

(2) Write a short essay on the validity of the second law of thermodynamics.

(3) Show that the greatest possible efficiency would be attained by a steam engine, if its working substance could be made to pass through a completely reversible cycle and heat was absorbed only at one temperature, and rejected only at one other temperature.

(4) Give an account of the doctrine of the dissipation of energy.

(5) Assuming that no thermal engine can be more efficient than one which works between the same temperatures in a simple reversible cycle, explain the construction of the scale of absolute temperatures.

(6) Assuming that all reversible engines going round a Carnot's cycle between two given temperatures are equally efficient, show how a work scale of temperature may be devised which is independent of any particular material used, and show, by taking a gas round a small cycle, that the gas scale nearly agrees with the work scale.

(7) What do you understand exactly by the efficiency of a steam engine? What is the theoretical efficiency of a steam engine whose boiler is at 150° C. and its condenser at 40°?

(8) A heat engine works between the temperatures 127° and 52° C. It is found that only one-third of the largest amount of heat that could possibly be utilised is actually converted into useful work. What fraction of the total amount of heat supplied is usefully employed?

(9) Enunciate the axiom on which the second law of thermodynamics rests, and show how to deduce from it a proof of the fact that the efficiency of a simple reversible cycle is a maximum.

CHAPTER XVII

APPLICATIONS OF CARNOT'S THEOREM

External and Internal Latent Heats.—As a general rule, a considerable change of volume occurs whilst a substance is changing its state. This is very noticeable in the case of the conversion of water into steam at the same temperature. Thus at atmospheric pressure, one volume of water at 100° C. is converted into 1,647 volumes of saturated steam at the same temperature. During such a process external work is performed, and the total heat absorbed (*i.e.*, the latent heat of the substance) is equal to the sum of the increase in the intrinsic energy of the substance (sometimes called the "true latent heat"), and the external work performed. This latter quantity is called the "external latent heat."

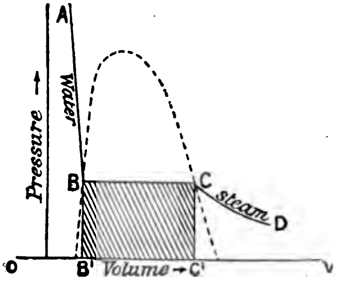

Fig. 161.—Work performed during vaporisation of water.

Let ABCD represent the 100° C. isothermal for one gram of water and steam. Let us suppose that the water is inclosed in a cylinder provided with conducting walls. At the point B it entirely fills this cylinder. Along the line BC the pressure remains constant, but as the water is converted into steam the volume increases from OB' to OC'. Hence the piston is forced outwards against the atmospheric pressure, and an amount of external work equal to the area BCC′B′ is performed.

The latent heat of steam at 100° C. = 537 therms per gram.

Work performed during expansion from 1 c.c. to 1,647 c.cs. = W

= atmospheric pressure (in dynes) × increase of volume (in c.cs.)

$= 76{\cdot}0 \times 13{\cdot}6 \times 981 \times 1{,}646 = 1{\cdot}67 \times 10^9$ ergs.

$$\text{Heat used up in performing external work} = \frac{W}{J}$$

$$= \frac{1{\cdot}67 \times 10^9}{4{\cdot}2 \times 10^7} = 39{\cdot}7 \text{ therms.}$$

∴ External latent heat of water boiling under atmospheric pressure = 39·7 therms per gram.

Internal latent heat of water at 100° = 537 − 39·7 = 497·3 therms per gram.

Similar reasoning will apply to the passage from the solid to the liquid state, though here, in the case of water, a contraction occurs, so that the external latent heat is negative. The volume change associated with the passage from the solid to the liquid state is generally small in comparison with that which occurs during the conversion of a liquid into vapour.

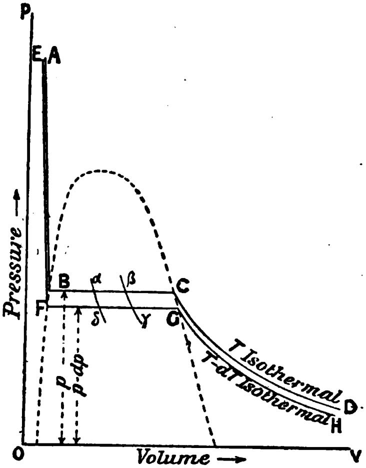

FIG. 162.—Cycle performed to determine the elevation of the boiling point of a liquid by an increase of pressure.

To Calculate the Depression of the Boiling Point produced by a given Diminution of Pressure.—Let us suppose that any quantity of the specified substance is enclosed in the cylinder of an ideal heat engine, such as that described on p. 333. Let ABCD, EFGH (Fig. 162), be the isothermals of this substance for temperatures T and T − *d*T, where *d*T is small. Along the lines BC and FG the substance exists partly in the state of liquid and partly in the state of vapour. Hence T is the boiling point of the substance, under the pressure p corresponding to the vertical height of the line BC above the axis of volume OV. Similarly $T-dT$ is the boiling point under a pressure $p-dp$, where dp is the vertical distance between the lines BC and FG.

Let us start with the substance at the temperature T, and in the condition represented by the point β, and perform the following operations :—

1. Place the cylinder on the non-conducting stand, and allow its contents to expand adiabatically till the temperature falls to $T-dT$. The point γ is thus reached.

2. Place the cylinder on a conducting stand maintained at the constant temperature $T-dT$, and compress the substance isothermally till any point δ, not far removed from γ on the line FG, is reached. Let Q_2 be the heat given up during this process.

3. Place the cylinder on the non-conducting stand, and compress the substance adiabatically till its temperature rises to T. The condition now attained corresponds to the point a.

4. Place the cylinder on a conducting stand maintained at the constant temperature T, and allow the substance to expand isothermally, till its original condition is reached. Let Q_1 be the heat absorbed during this process.

We have thus performed a cycle of operations. This cycle is reversible, since it is obvious that it could have been traversed in the sense $\beta a\delta\gamma\beta$, subject to the conditions prescribed on p. 335.

In the direct cycle, we have the following relations :—

External work performed during the cycle = area $a\beta\gamma\delta$ (p. 338).

Heat converted into work $= Q_1 - Q_2 =$

$$\frac{\text{Area } a\beta\gamma\delta}{J}. \quad \text{(First law of Thermodynamics.)}$$

Efficiency of the heat engine, working between temperatures T and $T-dT$ =

$$\frac{Q_1-Q_2}{Q_1} = \frac{\dfrac{\text{Area } a\beta\gamma\delta}{J}}{Q_1} = \frac{T-(T-dT)}{T} = \frac{dT}{T} \quad . \quad . \quad . \quad (1).$$

(This relation depends on Carnot's theorem, together with the reasoning employed on pp. 345 to 351. T is the absolute temperature measured on a "perfect gas" thermometer.)

It is not necessary to know the exact form of the adiabatic curves $\beta\gamma$ and $a\delta$. For if a and β are close together, we may safely assume that $a\delta$ will be approximately parallel to $\beta\gamma$. Also; $a\beta$ is parallel to $\delta\gamma$.

Therefore, the area of the parallelogram $\alpha\beta\gamma\delta = \alpha\beta \times$ vertical distance between $\alpha\beta$ and $\delta\gamma = \alpha\beta \times dp$.

But $\alpha\beta$ is equal to the increase in volume between the points α and β. The value of this increase in volume may be best obtained from considering the mass of liquid which has been vaporised.

Let m be the mass of liquid vaporised between α and β.

Let v_1 be the specific volume (*i.e.*, the volume occupied by 1 gram) of the liquid, at a temperature T.

Let v_2 be the specific volume of the saturated vapour at a temperature T (p. 254).

Then a mass m of the substance would occupy a volume mv_1 in the liquid state and mv_2 in the state of vapour.

Therefore, since a volume mv_1 of liquid has been replaced by a volume mv_2 of saturated vapour, the increase in volume $(=\alpha\beta) = m(v_2 - v_1)$.

Therefore,

$$\text{area } \alpha\beta\gamma\delta = m(v_2 - v_1) \times dp.$$

The only other quantity which must be determined is Q_1, the heat absorbed in passing from α to β.

In this case, since part of the substance changes state between α and β, heat will be absorbed (1) in altering the state of part of the substance, and (2) in performing external work.

If L = the heat required to vaporise 1 gram of the substance at the temperature T, we have

$$Q_1 = mL.$$

Substituting in (1) the values thus found, we get

$$\frac{m(v_2 - v_1)\,dp}{mLJ} = \frac{(v_2 - v_1)\,dp}{LJ} = \frac{dT}{T}$$

$$\therefore\ dT = \frac{T(v_2 - v_1)\,dp}{LJ}$$

In the above, dT is the depression of the boiling point produced by a diminution of pressure equal to dp, and this is the quantity we wished to determine.

Application to the case of Water.

Put $dp = 1$ mm. of mercury $= \cdot 1 \times 13\cdot 6 \times 981$ dynes.

One gram of water at 100° C. occupies a volume of 1·04 c.c.

∴ One gram of steam at 100° C. occupies a volume of 1,647 c.cs.

$$v_2 - v_1 = 1{,}646 \text{ nearly}.$$

∴ $T = 273 + 100 = 373$.

∴ Depression of the boiling point for a decrease of pressure of 1 mm

$$= dT = \frac{373 \times 1{,}646 \times \cdot 1 \times 13\cdot 6 \times 981}{537 \times 4\cdot 2 \times 10^7} = \cdot 0364^\circ \text{ C.}$$

The value obtained by experiment is ·037° C.

To calculate the alteration in the melting point produced by a given increase of pressure.

The form of the isothermals representing the relation between pressure, volume, and temperature of a substance during melting will be similar to ABCD, EFGH, Fig. 162, *provided an increase of volume occurs on melting*. (For complete isothermals of such a substance, *see* Fig. 120, p. 237.)

Let us suppose that a cylinder is filled with a mixture of the solid and liquid. Starting with this mixture in the condition represented by the point β, we may traverse the cycle $\beta\gamma\delta\alpha\beta$ as already explained, and the formula ultimately obtained, viz.

$$dT = \frac{T(v_2 - v_1)dp}{LJ}$$

will express the depression of the melting point due to a decrease of pressure dp. In this case

L = the latent heat of fusion of the solid.
v_1 = the volume occupied by 1 gram of the solid.
v_2 = the volume occupied by 1 gram of the liquid.

Application to the case of Paraffin Wax.—In the case of paraffin wax, a substance which expands on melting, we have the following data:—

L = latent heat of fusion = 35·35 therms per gram.
$v_2 - v_1$ = increase in volume of 1 gram on fusion = 0·125 c.cs.
Melting point = 52·7° C.
$\therefore T = 273 + 52{\cdot}7 = 325{\cdot}7.$

Take dp = the pressure (in dynes) corresponding to 1 atmosphere.

$$dp = 76{\cdot}0 \times 13{\cdot}6 \times 981 = 1{\cdot}01 \times 10^6 \text{ dynes.}$$

$$\therefore dT = \frac{325{\cdot}7 \times {\cdot}125 \times 1{\cdot}01 \times 10^6}{35{\cdot}35 \times 4{\cdot}27 \times 10^7} = {\cdot}027^\circ \text{ C.}$$

Hence, according to this calculation, the melting point of paraffin wax will be depressed by ·027° C. due to a diminution of pressure amounting to 1 atmosphere.

Therefore the melting point of paraffin will be *raised* by ·027° C. if the pressure to which it is subjected is *increased* by 1 atmosphere.

M. Batelli[1] has found experimentally that the melting point of paraffin wax is raised by ·03° C. when the pressure to which it is subjected is increased by 1 atmosphere.

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[1] M. Batelli, *Journal de Physique*, tom. vi. p. 90. 1887.

Application to the case of Ice.—In this case a contraction occurs on melting. Let AB and CD, Fig. 163, represent portions of the isothermals corresponding to the melting points of ice under pressures of p and $p - dp$ dynes. (For complete isothermals of ice, water, and aqueous vapour, *see* Fig. 121, p. 238.) Let AB correspond to a temperature T_1, and CD to a temperature T_2. We must determine whether T_1 is greater than T_2, or the reverse.

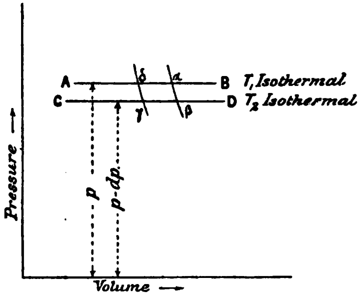

FIG. 163.—Cycle performed to determine the depression of the freezing point of water under increased pressure.

Let us suppose the cylinder of an ideal heat engine to be filled with a mixture of ice and water at a temperature T_1, corresponding to the melting point of ice when subjected to the pressure p which is exerted on the piston. Let the initial condition of the contents of the cylinder be represented by the point α, Fig. 163.

Now perform the following operations:—

1. Place the cylinder on the non-conducting stand and cause the condition of its contents to change adiabatically till the pressure falls to $p - dp$. Note the temperature T_2 attained. An adiabatic, such as $\alpha\beta$, is thus traversed.

2. Place the cylinder on a conducting stand maintained at a temperature T_2, and cause its contents to contract isothermally till a mass m of ice has been converted into water. During this operation a quantity of heat equal to Lm (where L is the latent heat of fusion of ice) will have been absorbed at the temperature T_2. The condition of the substance will now correspond to the point γ.

3. Place the cylinder on the non-conducting stand, and cause the condition of its contents to change adiabatically till the initial temperature T_1 is attained. An adiabatic $\gamma\delta$ will thus be traversed.

4. Place the cylinder on a conducting stand maintained at the temperature T_1, and cause the contents to expand isothermally till their initial condition, represented by the point α, is attained. In order that a mixture of ice and water should expand, the temperature of the

mixture meanwhile remaining constant, a quantity of water must be converted into ice; and therefore a quantity of heat, equal to the product of the mass of the water frozen into the latent heat of ice, must have been given up.

We have now performed a cycle of operations, and that cycle is obviously reversible. Hence we may use Carnot's theorem in examining the results obtained.

Note the following points :—

A. Since the expansion from δ to a is performed against a pressure p, and the contraction from β to γ was performed under the pressure $(p - dp)$, we have

External work performed in expansion from δ to $a = p \times \delta a$.

Work performed by external agency during the contraction from β to γ . . . . $=(p - dp)\ \gamma\beta$.

Since δ and a are supposed to be close together, we may assume that the adiabatics $a\beta$ and $\delta\gamma$ are parallel.

$$\therefore\ \delta a = \gamma\beta.$$

$\therefore$ External work performed by the engine, *minus* work performed on the engine by external agency $= p \times \delta a - (p - dp) \times \gamma\beta$

$$= p \times \gamma\beta - (p - dp)\gamma\beta = dp \times \gamma\beta.$$

That is, a net quantity of external work equal to $dp \times \gamma\beta$ has been performed during the cycle.

B. But according to the second law of thermodynamics, *external work can only be performed when heat is absorbed at a high, and rejected at a lower temperature.*

In the present case, heat was absorbed during the passage from β to γ, at a temperature T_2, whilst heat was given up during the passage from δ to a.

Therefore T_2 is greater than T_1; in other words,

Ice melts at a higher temperature when subjected to a pressure p − dp, than it does when subjected to a pressure p.

We can now apply the relation

$$\frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} \quad . \quad . \quad . \quad . \quad (1)$$

where Q_2 is the heat absorbed at the higher temperature, T_2 and Q_1 is the heat rejected at the lower temperature T_1.

By the first law of thermodynamics $(Q_2 - Q_1)$ will be equivalent to the external work performed, *i.e.*, to the area $\alpha\beta\gamma\delta = dp \times \beta\gamma$.

Let v_1 = the volume occupied by 1 gram of ice at $T_2°$ (absolute).
,, v_2 = ,, ,, ,, ,, water at $T_2°$,,

Then, during the passage from β to γ, m grams of ice were melted. Therefore, mv_1 c.cs. of ice were replaced by mv_2 c.cs. of water.

$\therefore$ Diminution of volume = length $\beta\gamma = m(v_1 - v_2)$.

$\therefore$ Net external work performed during the complete cycle = area of cycle $= m(v_1 - v_2)dp$.

$$\therefore Q_2 - Q_1 = \frac{m(v_1 - v_2)\,dp}{J}.$$

Q_2 is the heat absorbed during the melting of m grams of ice, and is therefore equal to mL.

$$\therefore \frac{\frac{m(v_1 - v_2)dp}{J}}{mL} = \frac{(v_1 - v_2)\,dp}{JL} = \frac{T_2 - T_1}{T_2} \text{ from (1)}$$

But $T_2 - T_1$ is the elevation of the melting point of ice when the pressure is diminished from p to $p - dp$. Write $T_2 - T_1 = dT$.

$$\therefore dT = \frac{T_2(v_1 - v_2)\,dp}{JL}.$$

Note.—In the formula obtained on p. 371, dT represents the *depression* of the boiling point, when the pressure is diminished from p to $p - dp$. In that case v_2 was greater than v_1.

If, however, we suppose that $v_1 > v_2$, we shall obtain a negative value for dT, *i.e.*, the boiling point would be *raised* by a decrease of pressure.

This would agree with the formula just obtained, where dT represents the *elevation* of the melting point produced by a diminution of pressure dp.

At 0° C. ($T_2 = 273$) 1 gram of water occupies a volume of 1·000116 c.cs. = 1 c.c. roughly.

$$\therefore v_2 = 1 \text{ c.c.}$$

At 0° C., 1 gram of ice occupies a volume of 1·087 c.cs.

$$\therefore v_1 = 1\cdot087 \text{ c.cs.}$$
$$v_1 - v_2 = \cdot087.$$
$$L = 80 \text{ therms per gram.}$$

If we take dp = 1 atmosphere = $1\cdot01 \times 10^6$ dynes, we find that the temperature at which ice would freeze if exposed to zero pressure, is given by

$$dT = \frac{273 \times {\cdot}087 \times 1{\cdot}01 \times 10^6}{80 \times 4{\cdot}27 \times 10^7} = {\cdot}0070^\circ \text{ C.}$$

Also, the freezing point of water will be lowered by ·0070° C. for each additional atmosphere of pressure applied to it.

Dewar found that the freezing point of water was depressed by ·0072° C. per atmosphere increase of pressure up to 700 atmospheres.

Problem.—A 20 horse-power non-condensing engine is supplied with steam at a temperature 150° C., and requires 120 lbs. of coal per hour; a 10 horse-power engine is supplied with steam at a temperature of 140° C., and requires 61 lbs. of coal per hour. Taking into consideration the greatest attainable efficiency of each engine, determine which is the most nearly perfect. (*B. Sc.* (*Lond.*) *Hons.*, 1889.)

$$\text{Actual efficiency} = \frac{\text{Heat equivalent of work performed}}{\text{Total heat supplied}} \quad . \; . \quad (1)$$

$$\text{Maximum efficiency} = \frac{T_1 - T_2}{T_1}.$$

In the 20 horse-power engine, $T_1 = 273 + 150 = 423$
$T_2 = 273 + 100 = 373$.

(The temperature of the exhaust steam is 100° C., since the engine is non-condensing, and thus steam is discharged at atmospheric pressure.)

$\therefore$ Maximum efficiency of the 20 horse-power engine $= \dfrac{423 - 373}{423}$

$$= \frac{50}{423} = {\cdot}118.$$

Similarly, maximum efficiency of the 10 horse-power engine =

$$\frac{(140 + 273) - (100 \div 273)}{140 + 273} = \frac{40}{413} = {\cdot}097 \text{ nearly.}$$

Let the quantity of heat supplied at the higher temperature = K × number of pounds of coal consumed, where K is a constant.

The 20 horse-power engine performs 20 × 33,000 ft.-lbs. of work per minute = 20 × 60 × 33,000 ft.-lbs. of work per hour.

The 10 horse-power engine performs 10 × 60 × 33,000 ft.-lbs. of work per hour.

Let J = the number of foot-pounds corresponding to one unit of heat.

Then actual efficiency of the 20 horse-power engine

$$= \frac{20 \times 60 \times 33{,}000 \div J}{K \times 120} = \frac{330{,}000}{JK}.$$

Actual efficiency of the 10 horse-power engine

$$= \frac{10 \times 60 \times 33{,}000 \div J}{K \times 61} = \frac{325{,}000}{JK}.$$

∴ in the case of the 20 horse-power engine

$$\frac{\text{Actual efficiency}}{\text{Maximum efficiency}} = \frac{\frac{330{,}000}{JK}}{\cdot 118} = \frac{2{,}800{,}000}{JK}.$$

In the case of the 10 horse-power engine

$$\frac{\text{Actual efficiency}}{\text{Maximum efficiency}} = \frac{\frac{325{,}000}{JK}}{\cdot 097} = \frac{3{,}350{,}000}{JK}.$$

Therefore the 10 horse-power engine is more nearly perfect than the 20 horse-power engine.

Problem.—What is the efficiency of a locomotive engine which requires 1,200 lbs. of coal per hour, when drawing a train against frictional forces, equivalent to the weight of 1½ tons, at the rate of 40 miles per hour?

If the engine is non-condensing, what must be the temperature of the steam in the boiler, supposing the construction of the engine to be perfect.

Given.—The combustion of 1 lb. of coal generates sufficient heat to raise the temperature of 15,580 lbs. of water through 1° F. The expenditure of 780 ft.-lbs. of work will raise the temperature of 1 lb. of water through 1° F. ∴ $J = 780$.

Using the pound, foot, and Fahrenheit degree as units, we have

Work performed while the engine traverses 1 mile = Force (in pounds) equivalent to 1½ tons × distance (in feet) equal to 1 mile

$$= \frac{3}{2} \times 2{,}240 \times 1{,}760 \times 3 = 1 \cdot 77 \times 10^7 \text{ ft.-lbs.}$$

The engine traverses 1 mile in $\frac{1}{40}$ hour, and consumes $\frac{1{,}200}{40} = 30$ lbs. of coal in that interval.

Quantity of heat generated = 15,580 × 30 = 467,400 pound-Fahrenheit-degree units.

$$\therefore \frac{\text{Heat equivalent to the work performed}}{\text{Heat supplied by combustion of coal}} = \frac{\frac{1 \cdot 77 \times 10^7}{780}}{467{,}400}$$

$$= \cdot 046, \textit{ i.e.}, 4 \cdot 6 \text{ per cent.}$$

Since the engine is non-condensing, $T_2 = 273 + 100 = 373$. Let T_1 be the absolute temperature of the steam in the boiler.

Then

$$\frac{T_1 - 373}{T_1} = 0{\cdot}046.$$

$$1 - \frac{373}{T_1} = 0{\cdot}046 \therefore \frac{373}{T_1} = 1 - 0{\cdot}046 = 0{\cdot}954.$$

$$\therefore T_1 = \frac{373}{{\cdot}954} = 391^\circ.$$

∴ Temperature of steam in boiler = 391° − 273 = 118° C.

For method of determining the absolute zero of temperature from the porous plug experiment, see Appendix, p. 481.

Summary to Chapter XVII.

External Latent Heat.—During a change of state, external work must be performed if a change of volume occurs. The heat equivalent of this work is called the external latent heat of the substance.

By taking a mixture of water and steam round a Carnot's Cycle an expression can be obtained for the elevation of the boiling point, when the pressure is increased.

The Efficiency of a Steam Engine cannot possibly exceed the theoretical efficiency of an ideal heat engine traversing a Carnot's Cycle, and absorbing heat at the temperature of the boiler, and rejecting heat at the temperature of the condenser.

Actual Steam Engines always fall short of this theoretical efficiency either on account of irreversible thermal effects, or because heat is not wholly absorbed at one temperature, and rejected at another temperature.

Questions on Chapter XVII.

(1) Describe what effect is produced by pressure in changing the temperature of the freezing point of water, and state how this change is explained on the principles of conservation of energy.

(2) Discuss the method of calculating the relation between the melting point of ice and the pressure.

(3) The latent heat of steam at 100° C. is 536. If a kilogram of water, when converted into saturated steam at atmospheric pressure, occupies 1·651 cubic metres, calculate the amount of heat spent in internal work during the conversion of water at 100° C. into steam at the same temperature.

(4) Describe and give a general explanation of the thermal effects of compressing suddenly (1) a gas, (2) water at a temperature between 0° and 4° C.

CHAPTER XVIII

INTERNAL WORK, AND THE COOLING OF GASES ON FREE EXPANSION

Joule's Experiment.—In Chap. XIII., when considering the results which might be anticipated from the Kinetic Theory of gases, the question arose, is internal work performed during the separation of the molecules which occurs during the expansion of a gas? An experiment of Joule's was then described; in this, a quantity of gas contained in a vessel under high pressure, was allowed to expand into another vessel which had been exhausted. Both vessels were, in the first experiment, surrounded by water contained in the same calorimeter.

In this experiment, no external work was performed by the gas during expansion. The gas expanding in one vessel compresses the gas contained in the other vessel. Thus, a cooling effect might be anticipated in the first vessel, and a heating effect in the second one. At the end of the experiment the gas occupied a greater volume than at first; and if, after stirring the water in the calorimeter, its final temperature is found to be unchanged, we must conclude that no appreciable amount of work has been performed during the separation of the molecules; or, in other words, that the average attraction or repulsion exerted by one molecule on another is very small.

Joule's experiment led to the result just stated. It must, however, be remembered that if a small heating or cooling, say through a fraction of a degree, does really occur when a gas expands without doing external work, the quantity of heat given out (or absorbed) will be so small that little change will be produced in surrounding bodies. Hence, Joule's experiment must only be taken as proving that no heating or cooling effect *of any considerable magnitude* occurs during the free expansion of the ordinary gases.

The weak point in Joule's experiment was unquestionably the use of water to indicate, by its change of temperature, whether heat disappeared or was generated in the expanding gas. The specific heat of air at constant volume, according to Joly, is equal to ·1721 therms per gram. Now a gram of air, at 0° C. and under atmospheric pressure, will occupy a volume of 773·4 c.cs. The heat required to raise the temperature of this volume of air through 1° C., if abstracted from a gram of water, would only cool the latter through ·17° C. Thus, though Joule's thermometer was capable of indicating a difference of temperature of $\frac{1}{200}$° F. ($\frac{1}{360}$° C.) it is obvious that no heating or cooling effect, unless of a considerable magnitude, could possibly have been detected by the method he employed.

Investigation of Joule and Lord Kelvin.—Thermodynamical considerations lead to the conclusion that whereas there should be no heating or cooling of a perfect gas on free expansion, gases which do not obey Boyle's Law should exhibit a small thermal change under the same conditions. Lord Kelvin and Joule therefore determined to investigate the phenomena attending the free expansion of gases, using a method in which the temperature of the gases could be directly measured.

Before describing the actual experiment performed by Joule and Lord Kelvin, we will consider an ideal arrangement illustrating the character of the process employed.

Let us suppose that we are provided with a long cylinder CD, fitted with two air-tight and frictionless pistons, A and B, and possessing a diaphragm E pierced by a small aperture.

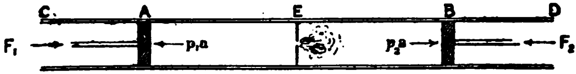

FIG. 164.—Gas forced through narrow orifice under pressure.

Let us suppose that the piston B is initially pressed close up to the diaphragm E, whilst a certain quantity (say 1 gram) of compressed gas, at a pressure p_1, is introduced into the part of the cylinder between

A and E. We must further assume that the walls of the cylinder are perfect non-conductors of heat. Thus, if T is the initial temperature of the gas, any departure from this value can only be produced by the performance of work on or by the air, and not by the direct transference of heat.

Now let the motion of the piston B be opposed by a uniform force F_2.

Let a be the area of either piston. Then the piston B will move outward uniformly when the pressure of the gas between E and B has attained such a value p_2 that

$$p_2a = F_2.$$

Also let the force, tending from the first to force the piston A inwards, be denoted by F_1. Then, as the gas passes through the orifice in E, so as to press the piston B forwards, the piston A will move inwards towards E at such a rate that the pressure p_1 of the air between A and E remains constant. Then

$$p_1a = F_1.$$

Let us suppose that the gas initially contained in AE occupied a volume v_1. Also let x_1 denote the distance between the piston A and the diaphragm E at the commencement of the experiment. Then

$$ax_1 = v_1.$$

When the piston A has moved up to the diaphragm E, the whole of the air will have been forced from the compartment AE into the compartment EB of the cylinder. Let v_2 be the volume occupied by the air in EB, and let x_2 be the distance through which the piston B has meanwhile moved, from its initial position immediately against the diaphragm E. Then

$$ax_2 = v_2.$$

No heat can enter or leave the cylinder, so that any change in the energy of the contained gas must be due to the performance of work on or by it.

Let E_1 be the internal energy possessed by the gas when in AE, and let E_2 be the internal energy possessed by it in EB.

The work performed by external agency *on* the gas is equal to the product of the force F_1 into the distance x_1 through which it has acted.

$\therefore$ Work performed *on the gas*

$$= F_1 \times x_1 = p_1ax_1 = p_1v_1.$$

The work performed by the gas is equal to the product of the force resisting the motion of the piston B (*i.e.*, F_2) into the distance x_2 through which that force has been overcome.

$\therefore$ Work performed *by the gas*

$$= F_2 \times x_2 = p_2 a x_2 = p_2 v_2.$$

The difference, $E_2 - E_1$ between the final and initial energies of the gas, must be equal to the difference between the work performed *on* the gas, and that performed *by* it.

$$\therefore p_1 v_1 - p_2 v_2 = E_2 - E_1.$$

Now, the energy possessed by the molecules of the gas may be partly kinetic and partly potential. The kinetic energy we have learnt to associate with heat; the potential energy will depend on the relative mean positions of the molecules, supposing that attractive or repulsive forces are exerted between them.

We can now consider the following cases:—

I. $p_1 v_1 = p_2 v_2$ (*i.e.*, the gas obeys Boyle's Law).

In this case $E_1 = E_2$. If there is any attractive force exerted between neighbouring molecules, this force must have been overcome during the expansion of the gas, and consequently the potential energy of the molecules must be greater in the final than in the initial condition.

But the total energy has the same value in both cases. Therefore the kinetic energy of the gas is smaller in the final than in the initial condition. In other words, the gas will be cooled during the process described above.

If repulsive forces are exerted between neighbouring molecules, the potential energy of the molecules will be diminished during expansion, and consequently their kinetic energy will increase. In other words, the gas will be heated during the process described above.

II. $p_1 v_1 < p_2 v_2$. In this case the product of the pressure and volume of the gas decreases as the pressure is increased. This condition generally holds during the initial stages of the compression of a gas. Hydrogen is, however, an exception (*see* p. 204).

Since

$$p_1 v_1 - p_2 v_2 = E_2 - E_1$$
$$E_2 - E_1 = \text{some negative value} = -\xi \text{ (say)}$$
$$\therefore E_2 = E_1 - \xi$$

that is, the energy possessed by the gas is less in the final than in the initial condition.

Therefore, if no forces are exerted between neighbouring molecules, a slight cooling effect will be produced.

If molecular attractions are exerted, a still greater cooling will result.

If molecular repulsions are exerted, the cooling due to the divergence from Boyle's Law may be partially or entirely compensated for, or a heating effect may be produced.

III. $p_1v_1 > p_2v_2$. In this case the product of the pressure and volume of the gas increases as the pressure is increased. Regnault and Amagat found this to be the case with hydrogen, and Amagat showed that it is also the case with most gases, when subjected to very high pressures.

Since
$$p_1v_1 - p_2v_2 = E_2 - E_1$$
$$E_2 - E_1 = \text{some positive value} = + \xi \text{ (say)}$$
$$\therefore E_2 = E_1 + \xi.$$

A heating effect will be produced if no molecular forces are exerted. This heating effect will be enhanced if molecular repulsions exist. If molecular attractions exist, a smaller heating effect or even a cooling effect, may be produced.

Modifications of the above Ideal Arrangement.—Returning to Fig 164, it may easily be understood that in the neighbourhood of the orifice in E the gas will form eddies. But any motion of finite portions of the gas will entail a diminution in the energy of molecular motion. Thus, near the orifice in F the gas will be colder than at points further removed, where the gas has been brought to rest by internal friction. Consequently, in performing an experiment such as that just described, care must be taken that the temperature of the gas is measured at a point where eddies have ceased to exist.

Further, the piston B may be dispensed with. It serves to divide the gas from the surrounding atmosphere; but if it is removed, the atmosphere will be forced back in an essentially similar manner; the pressure p_2 will then be equal to the atmospheric pressure.

Care must be taken that the jet of air issuing from the orifice in E does not produce any sound, as this would involve a loss of energy.

Instead of forcing the piston A along the cylinder, the end C of the latter may be connected to a pump, provided the action of the latter is such that the pressure of the gas, at all points to the left of the diaphragm E, is maintained constant. The essential point in the arrangement is that no change shall take place in the compressed gas till it passes through the orifice in E. Thus, the gas between E and the pump must be maintained at a constant temperature and pressure, and must serve to transmit the pressure, exerted by the pump, to the gas issuing through the orifice in E.

The Porous Plug Experiment.—We are now in a position to appreciate the experimental arrangement used by Joule and Lord Kelvin.

To avoid the production of eddy currents in the gas, a plug of cotton-wool A, Fig. 165, was substituted for the pierced diaphragm E, Fig. 164. By this means a large number of very small orifices was obtained, in place of the single orifice previously considered. The cotton-wool was held in position by two metal discs pierced with many holes; these discs are indicated by dotted lines in the figure. To avoid loss or gain of heat in the neighbourhood of the plug, the latter was enclosed in a hollow boxwood cylinder BC, which in its turn was surrounded by cotton-wool packed in a metal vessel D. The gas was conveyed to the plug by means of a metal tube E which formed the end of a long spiral tube, immersed in a water bath. A delicate thermometer was placed so that its bulb was immediately above the plug, and in order that the thermometer might be read, a glass tube F was used to convey the gas away.

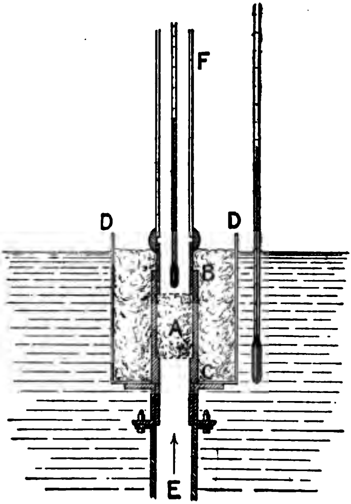

FIG. 165.—Joule and Kelvin's porous plug experiment.

The whole of the experimental arrangement is represented diagrammatically in Fig. 166. The gas was compressed by a pump P, and then caused to traverse two long copper spirals immersed in water baths. These baths were kept well stirred, and their temperatures were maintained constant throughout the experiment. During the time that the gas was being compressed in P, heat was produced, and the object of the baths was to keep the temperature of the gas as constant as possible. The part of the apparatus containing the cotton-wool plug is represented at A, Fig. 166.

Result of Joule and Kelvin's Experiment.—It was found that air, oxygen, nitrogen, and carbon dioxide were all cooled by expansion ; *i.e.*, after passing through the cotton-wool plug all of these gases were at lower temperatures than previously. The cooling was most noticeable in the case of carbon dioxide, the least perfect of the above gases. In the case of hydrogen, a small heating effect was observed.

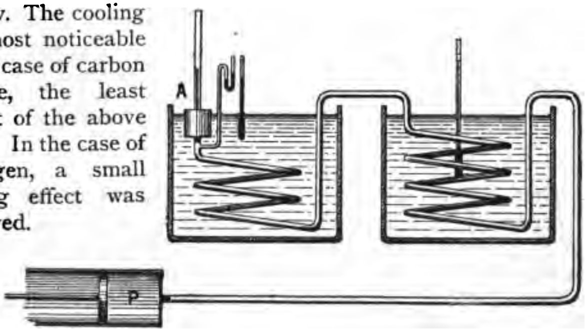

FIG. 166.—Joule and Kelvin's porous plug experiment.

In all cases the thermal effect produced was *proportional to the difference between the pressures on the two sides of the plug.* At high temperatures the cooling effect was less than at low temperatures. Its actual magnitude varied inversely as the square of the absolute temperature of the gas.

The following table embodies the results of Joule and Kelvin's experiments on air. It shows the value of the fall of temperature produced by free expansion, when the difference in pressure on the two sides of the plug is 1 atmosphere.

AIR.

Mean Temperature during Experiment.	No. of Experiments.	Fall in Temperature on Free Expansion, for a difference of pressure of 1 atmosphere.
7° C.	8	0·263° C.
26 ,,	2	0·229 ,,
50 ,,	6	0·209 ,,
93 ,,	6	0·152 ,,

Hydrogen.—In the case of hydrogen, a *rise* of temperature amounting to 0·039° C. per atmosphere difference of pressure on the two sides of the plug, was found to result.

Carbon Dioxide :

Mean Temperature.	No. of Experiments.	Fall in Temperature on Free Expansion, for a difference of pressure of 1 atmosphere.
8° C.	2	1·233° C.
36 ,,	1	1·022 ,,
54 ,,	1	0·885 ,,
96 ,,	2	0·645 ,,

Thus, if we let δ be understood to denote the thermal effect experienced by a gas when it is allowed to expand without doing external work, we see that δ is negative for air and carbon dioxide, and positive for hydrogen.

Conclusions.—The conclusions reached as a result of these experiments are :—

(1) That at ordinary temperatures, neighbouring molecules of air, nitrogen, oxygen, and carbon dioxide exert a small but appreciable attractive force on each other.

(2) As the temperature of a gas rises, the ratio of the potential to the kinetic energy of a molecule becomes smaller. This might have been anticipated, since at the same pressure, the mean distance between neighbouring molecules will increase with the temperature.

(3) The small heating effect noticed in the case of hydrogen may be due to the repulsion of its constituent molecules, or to some other cause as yet undetermined.

Dr. Linde's Apparatus for Liquefying Air.—We have seen above that when air issues from a small orifice, it experiences a fall in temperature amounting to about a quarter of a degree Centigrade for each atmosphere of difference in pressure between the two sides of the orifice. At first sight this small drop in temperature would not appear capable of utilisation in the attainment of very low temperatures (*e.g.*, – 200° C.). But methods based on the use of this fall in temperature possess the advantage that they can be rendered continuous.

Fig. 167[1] shows, in its simplest form, the arrangement adopted by Dr. Linde for this purpose.

Air is compressed in the pump P, and passes, by way of the tube HJB, through the water cooler KL. The heat generated during the compression of the air in the pump is thus removed. The compressed air then passes along the tube BC, and thence through the central tube of the "interchanger" CDE. The compressed air then escapes through the small orifice of the throttle valve R, into the vessel T. At this point a fall in temperature is experienced, and the air thus cooled passes back to the pump through the space between the central and outer tubes of the interchanger, and the tube CG. Thus, heat is abstracted from the air approaching the throttle valve, by the air which has previously been cooled there. Consequently the compressed air arriving at the throttle valve attains lower and lower temperatures as the pump is worked.

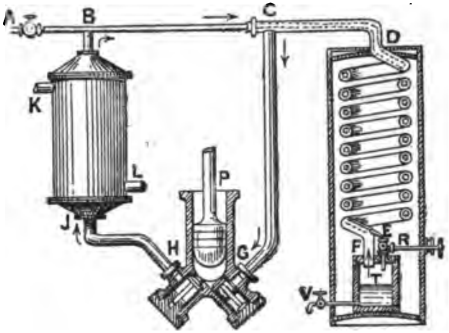

FIG. 167.—Linde's apparatus for liquefying air. (Early form.)

In May, 1895, after the pump had been working for fifteen hours, Dr. Linde was able to liquefy air by this method, no previous cooling having been employed.

Fig. 168 represents a rather more elaborate apparatus ; the principle of the action is, however, the same.

Compressed air is delivered by the pump *d*, by way of the tube p_2 and the refrigerator *g*, to the central tube at the top of the spiral interchanger. A mixture of ice and salt is used in the refrigerator *g*.

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[1] "Linde's Method of Producing Extreme Cold and Liquefying Air." By Prof. J. A. Ewing. *Journ. Soc. Arts*, March 11, 1898.

The compressed air then passes down through the central tube of the interchanger. All of the air passes through the throttle valve *a*, where the pressure drops from about 200 to 16 atmospheres; about $\frac{1}{5}$ of this air subsequently passes through the throttle valve *b*, where the pressure drops to a little more than an atmosphere. The remaining $\frac{4}{5}$ths of the air passes back between the central and the second tube of the interchanger, which, as shown in the figure, comprises three concentric tubes. It is finally brought back to the pump by the tube p_1.

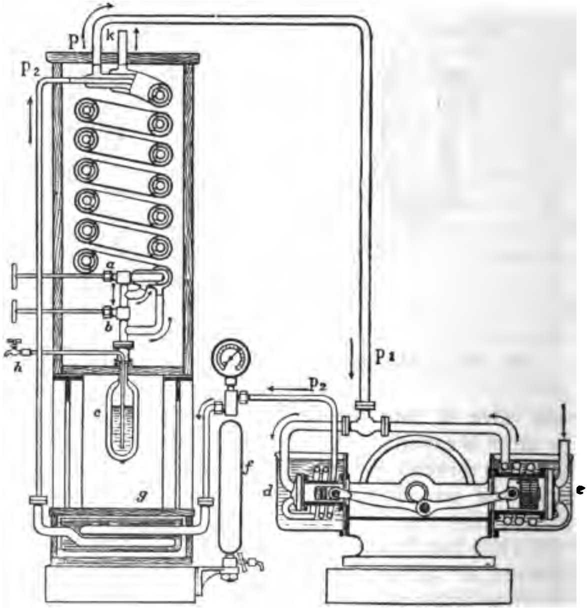

FIG. 168.—Linde's apparatus for liquefying air. (Later form.)

The air which has passed through the valve *b* passes into the vessel *c*, provided with a vacuum jacket. Part of this air is here liquefied, and the rest passes back between the second and outer tube of the interchanger, and escapes at *k* into the atmosphere. The space surrounding the interchanger is packed loosely with raw sheep's wool.

The pump *e* is used to compress air, obtained from the atmosphere, to 16 atmospheres, when it is delivered, together with the air returning by the tube p_1, to the pump *d*, whence it is caused to circulate as described.

Liquid air may be drawn off from the tap *h*. The machine represented in Fig. 168 is worked by a 3 horse-power engine, and produces a continuous supply of 0·9 litre of liquid air per hour. Fifteen cubic metres of air at 200 atmospheres are kept in constant circulation, and about 3 cubic metres are pumped in from outside in the same interval.

Further improvements have been made in this class of apparatus by Prof. Dewar and by Dr. W. Hampson. Liquid air can be obtained in a space of time as short as sixteen minutes, even when no previous cooling has been performed. If the air is first cooled by carbonic acid snow, liquid air may be obtained in two minutes.

Simple Method of Liquefying Oxygen.—When commenting on Dr. Linde's apparatus, after Prof. Ewing's lecture at the Society of Arts, Prof. Dewar[1] said :—"In order to get a small quantity of liquid air, all that was needed was to buy a bottle of compressed air at 200 atmospheres, take a small coil of copper pipe and put it into a vacuum vessel. By the use of a solid carbonic acid, it could be cooled to -80° C.; then expanding it through a small coil with a pin nozzle, 80 c.cs. of liquid air could easily be collected in twelve minutes, and after the nozzle had got cold, in half that time you could go on collecting from every 25 cubic feet that you expanded, practically, the same amount."

Liquefaction of Hydrogen.—This has been accomplished by Prof. Dewar. Hydrogen was first cooled as much as possible by liquid carbon dioxide and liquid ethylene, and was then allowed to expand at a pin-hole nozzle at the end of a long coil of copper tube. The extra cooling produced by free expansion was utilised in cooling the unexpanded gas, and liquid hydrogen was finally obtained. This experiment is of much interest, as it shows that when hydrogen at a very low temperature is allowed to expand without performing work. cooling is produced. (*Cf.* Joule and Kelvin's result, p. 386.)

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[1] *Journ. Soc. Arts*, March 11, 1898, p. 383.

Unfounded Claims as to the Production and Utilisation of Liquid Air.—The daily papers have recently contained accounts of certain so-called discoveries and inventions hailing from America. For example, it has been stated that with a particular form of machine, three gallons of liquid air may be caused, without external assistance, to produce ten gallons of liquid air. According to this report, air is capable of liquefying itself. This would be a direct violation of the Second Law of Thermodynamics, which states that heat cannot be abstracted from the coldest of a series of bodies, unless work is performed by some external agency (see p. 366).

Liquid air may be produced at a price of 10*d.* a cubic foot or 1*d.* per lb. This liquid may be allowed to evaporate, and thus to perform work; but the energy so obtained would be about 200 times dearer than it would have been if an ordinary steam engine had been used.

Free Expansion of High Pressure Steam.—It is a curious fact that high pressure steam escaping from a small orifice will not burn the hand, whilst low pressure steam, which is at a lower temperature, will inflict serious injury to the skin.

In explaining this fact, it must be remembered that the cause of the injury inflicted by steam is to be traced to the great amount of heat rendered up by that substance during condensation. In cooling from 101° C. to 100° C. (without condensation), the heat rendered up by steam would be comparable with that given up by air during a similar fall of temperature, and this would do no damage to the skin. Hence, as long as steam remains dry, and does not condense on the skin, no burn will result. Now, steam saturated at 100° C. will readily condense, and thus produce burns.

On the other hand, saturated steam, under a high pressure, will be at a considerably higher temperature than 100° C. In issuing from a small orifice, the work of pressing the atmosphere back is performed by the steam still in the boiler. (Compare with the explanation of Joule and Kelvin's experiment, p .383.)

The steam is set in violent motion on issuing from the orifice, and consequently a cooling will occur. But this steam is quickly brought to rest by friction with the surrounding air, and the heat previously lost is thus regained. Consequently the steam after issuing from the orifice will be at the same temperature as the steam in the boiler, except for the small cooling which takes place on free expansion. It will therefore be unsaturated, and in a perfectly dry condition. In fact, supposing the condition of the steam before issuing into the air to be represented by the extreme point to the right of the straight portion of the isothermal (Fig. 97, p. 208), its final condition, corresponding to a smaller pressure, will be represented by a point on the unsaturated vapour isothermal for the same temperature.

When saturated steam performs external work during expansion, part of the steam is condensed; this was the case with the steam in Hirn's experiment (p. 331). In escaping into the atmospheres from a small orifice, no external work is performed *by the escaping steam*, hence condensation does not take place.

For the determination of the absolute zero of temperature by the aid of data supplied by the porous plug experiment, see p. 481.

SUMMARY.

In Joule's Experiment on the internal work performed by an expanding gas, the thermal capacities of the water and the gas were so unequal that great accuracy could not be anticipated.

Joule and Lord Kelvin subsequently investigated the same point by forcing the gas through a plug of cotton-wool and determining the consequent change of temperature of the gas. In this case, the work of overcoming the pressure of the atmosphere is performed by the engine, and any change of temperature which occurs can only be due to the performance of internal work during the expansion.

As a result it was found that air is cooled during the expansion by about ·25° C. per atmosphere difference of pressure on the two sides of the plug. Consequently neighbouring molecules of air exert a small, but appreciable, attractive force on each other.

The Thermal Effects of Free Expansion are greater at low than at high temperatures. At low temperatures the attractive forces between neighbouring molecules become more important owing to the closer proximity of the molecules.

In Linde's Apparatus for liquefying air, the small fall of temperature due to the free expansion of the gas is utilised. After expanding through a small aperture, the cooled air abstracts heat from the air which has not yet expanded. This method is termed *self intensive.*

Prof. Dewar has suceeded in liquefying hydrogen by first cooling it as much as possible, and then allowing it to expand in a manner similar to that used by Linde. At high temperatures hydrogen is heated by free expansion. Dewar's experiments prove that at low temperatures hydrogen is cooled during free expansion.

QUESTIONS ON CHAPTER XVIII.

(1) Describe a method of liquefying a refractory gas.

(2) Give a description of the methods employed in liquefying air or some other of the more permanent gases.

(3) Describe Thomson's and Joule's experiments on the internal work of an expanding gas, and state the conclusion at which they arrived.

(4) Write a short essay on the methods of maintaining refractory gases in the liquid state for relatively long periods of time, and the uses to which they may be put.

(5) Describe the processes which are necessary to liquefy oxygen.

(6) Water is forced through a porous plug under a pressure of 50 kilograms per sq. cm. above the atmospheric, and emerges with negligible velocity at the pressure of the atmosphere. Assuming that there is no loss or gain of heat from external sources, find the rise of temperature of the water, if 427 metre-kilograms are equivalent to 1 kilogram-calorie.

CHAPTER XIX

ELECTRICAL INSTRUMENTS

Construction of a Galvanometer.—A galvanometer is an instrument used to measure the strength of electrical currents. Sometimes a galvanometer is used only to indicate the existence or absence of very small currents.

For a description of the tangent galvanometer and other instruments for measuring the absolute magnitude of currents, the student is referred to works on electricity.

A brief description will here be given of certain sensitive galvanometers which are frequently used in experiments connected with the science of Heat.

In order to explain the nature of these instruments, some preliminary consideration of the action of electric currents on magnets becomes necessary.

Let us suppose that a conductor, through which an electric current is flowing in the direction of the arrow, Fig. 169, is placed above a pivoted magnetic needle, parallel to the direction *SN* in which the latter points when acted on only by the

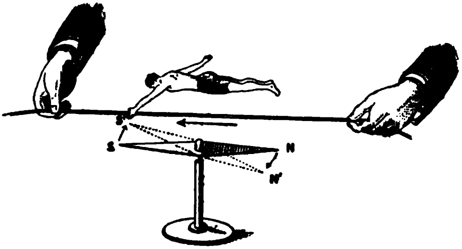

Fig. 169.—Deflection of a magnet by an electric current.

earth's magnetism. Then the magnetic needle will move to a position *S'N'*. The deflection of the magnetic needle will be increased as the conductor is brought nearer to the needle. Ampère's rule for determining the direction in which the respective poles of a magnet will move, when an electric current flows through a conductor in its neighbourhood, may be stated as follows.

Imagine a man to be swimming in the neighbourhood of the conductor in the direction pursued by the current. Let him turn so as to face the magnetic needle. Then the **S** pole of the latter will be deflected towards his **right** hand, the **N** pole being deflected towards his **left** hand.

If we imagine the conductor shown in Fig. 169 to be placed below the needle, the current flowing in the same direction as before, then remembering that the swimmer will still have his head pointing in the same direction, but will now be swimming face upwards, it can be seen that the needle will be deflected in an opposite direction to that shown in the figure.

If, however, when the conductor is placed below the needle, the current is reversed, the deflection of the needle will be in the same direction as that produced by the original current flowing above the needle.

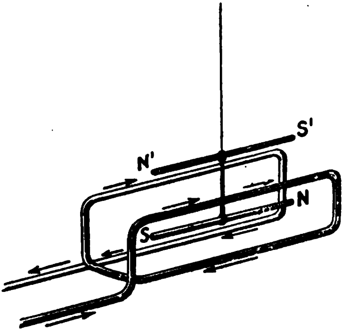

FIG. 170.—Simple astatic galvanometer.

Let us suppose that we have a piece of copper wire, bent into two rectangular loops as shown in Fig. 170. Let a magnetic needle *SN* be suspended by a fine fibre, so as to hang between and parallel to the planes of the loops. Then if an electric current is caused to flow along the wire, it will pursue opposite courses in the conductors above and below the needle. Hence, the deflection of the needle, produced by the current flowing along the conductors above it, will be increased by the action of the current flowing in the reverse direction along the conductors below it.

If a second needle, *N′S′*, with its poles oppositely directed to those of *SN*, be attached to the latter in such a position that it hangs above the upper conductors, it can be seen that the current in the upper conductors will tend to displace this needle in the same direction as that in which *SN* was displaced.

Two magnetic needles placed parallel to each other in the same plane, and with their poles oppositely directed, are said to form an *astatic combination.* Such a combination will be acted on by the earth's field to only a small extent. When suspended between two loops of wire in the manner indicated by Fig. 170, a current through the latter will produce a much greater deflection than if only one needle had been used.

The Astatic Galvanometer.—If we suppose that the two rectangular loops shown in Fig. 170 are replaced by two rectangular coils of many turns, we shall have a clear idea of the nature of Nobili's astatic galvanometer. This latter instrument is represented in Fig. 171. The upper magnetic needle moves over a graduated card, so that the deflection of the astatic system can be accurately observed. The ends of the wire forming the coils are joined to two terminals, and the base of the instrument is provided with levelling screws. A glass shade protects the suspended system from air draughts. It is arranged that the magnetic needles hang parallel to the planes of the coils when no current is passing through the galvanometer. It may be noticed that the longer the pointer which moves over the graduated card is, the smaller will be the angular deflection that can be observed.

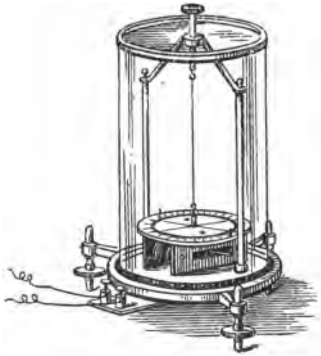

FIG. 171.—Nobili's astatic galvanometer.

The Reflecting Galvanometer.—If a galvanometer is required to indicate very small currents, the suspended system must be made very light. In this case a difficulty arises in obtaining a pointer of sufficient length which will yet possess no appreciable mass. This difficulty has been overcome by Lord Kelvin, by using a beam of light as a pointer.

Light from an oil lamp passes through a small aperture, and falls on a small silvered mirror attached to the suspended magnets. The light is thus reflected back, and falls on a scale placed above the aperture through which the light originally came. (Fig. 172.)

Small pieces of magnetised watch spring are used as magnets; these are fastened to the back of the small mirror, which in its turn is suspended by a fine fibre so as to hang between the coils of the galvanometer. A permanent magnet, supported on a vertical pillar fixed to the top of the galvanometer, serves to direct the small magnets.

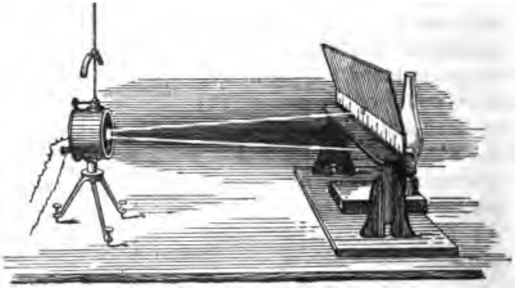

FIG. 172.—Reflecting galvanometer, with lamp and scale.

When a current passes through the coils, and the magnets, together with the attached mirror, are deflected through a given angle, the beam of light reflected from the mirror is deflected through twice that angle.

If the distance between the galvanometer and scale is equal to 1 metre, then a deflection of the mirror amounting to 1° will cause the spot of light on the scale to move through about 3·5 cms. As a motion of the spot of light on the scale can be observed to within ·01 cm., it follows that a deflection of the magnets amounting only to $\frac{1}{360}$° can be observed.

For most practical purposes, the distance through which the spot of light moves may be taken as proportional to the current flowing through the galvanometer coils.

The Suspended Coil Galvanometer.—The great drawback in the use of galvanometers of the suspended magnet type, lies in the fact that if magnets or pieces of iron are brought near them, a deflection may be produced. With sensitive instruments of this type, it is necessary for the experimenter to remove all keys, &c., from his pockets, and even when all possible precautions of this kind have been taken, any variations in the current carried by electric light mains in the neighbourhood of the instrument will alter the deflection of the needle.

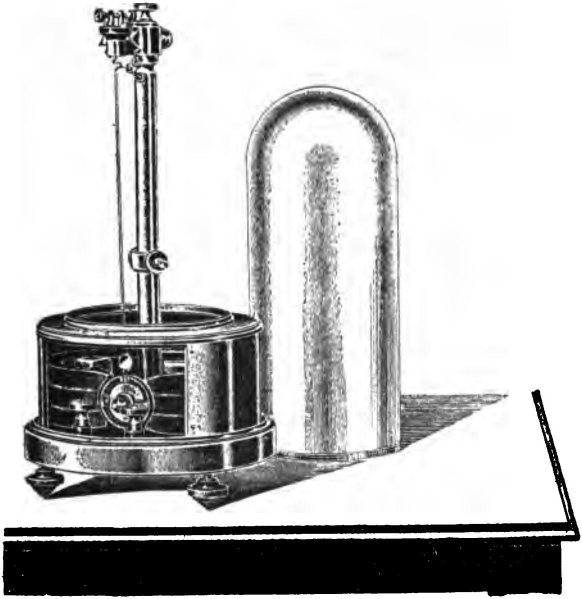

FIG. 173.—Crompton suspended coil galvanometer.

Difficulties such as those described may be entirely overcome by the use of a suspended coil galvanometer. If a coil is hung between the poles of a permanent magnet, the plane of the coil being parallel to the line joining the magnet poles, then a current sent through the coil will cause the latter to be deflected, just as the needle is in the case of an ordinary galvanometer.

Fig. 173 represents a suspended coil galvanometer made by Messrs. Crompton and Co. In this instrument a coil of fine wire is suspended, by the aid of two very thin and narrow metallic strips, so that it hangs between the poles of a powerful permanent magnet. The current is conveyed to and from the coil by way of the suspending strips. The strength of the permanent magnet is so great that bringing an ordinary magnet near will not produce any appreciable effect on the suspended coil when carrying a current. Hence magnetic disturbances are almost completely done away with in this type of instrument.

Comparison of Electrical Resistances.—Let us suppose that we are provided with three sets of coils, the electrical resistances of which, R_2, R_3, and R_4, can be adjusted at will to possess any required values. Let it be required to determine the resistances R_1 of some other coil. Connect the coils together, as shown in Fig. 174, by means of stout strips of copper, *abc*, *def*, *ghk*, *lmn*. Connect the terminals of a cell, V, to the points m and e, a key, K_1, being included in the circuit, so that the current can be interrupted when necessary. This key will be termed the battery key.

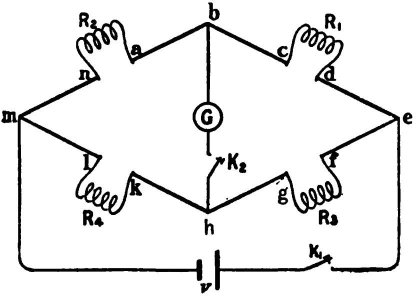

FIG. 174.—Diagrammatic representation of Wheatstone's bridge.

Connect the points b and h to the terminals of a sensitive galvanometer, G, a key, K_2, being also included in the circuit.

Then, if the resistances of R_2, R_3, and R_4, are so adjusted that when the keys K_1 and K_2 are successively depressed no deflection is produced in the galvanometer, we have the following relation

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}. \qquad \therefore R_1 = R_2\frac{R_3}{R_4}$$

Thus, if R_2 is known, and the ratio $\frac{R_3}{R_4}$ is also known, the value of R_1 can at once be obtained.

The above arrangement for comparing resistances is generally known as Wheatstone's Bridge. It was really, however, invented by Mr. S. Hunter Christie, and the invention was duly acknowledged by the late Sir Charles Wheatstone.

Electrical Methods of Measuring Temperature.—A mercury thermometer, as previously pointed out, is unsuitable for making measurements of very high temperature. It is equally unsuitable for measuring very low temperatures (those below −39° C., the freezing point of mercury). It is now possible to obtain in the laboratory temperatures as low as −245° C.; consequently some method of measuring such low temperatures becomes necessary.

As a matter of fact, a gas thermometer is in all cases used as an ultimate standard; but, as the use of such an instrument is somewhat tedious, besides demanding experimental conditions which cannot always be complied with, other methods of measuring very low or very high temperatures have been invented. The most important of these depend on the utilisation of certain electrical phenomena which vary with temperature.

Platinum Resistance Thermometer or Pyrometer.—The electrical resistance of a metallic wire varies with its temperature; consequently, we might utilise this property for the construction of a thermometer. For, if we calibrate the wire by determining its resistance at a sufficiently large number of temperatures, we may draw a curve connecting temperature and resistance, so that when the wire is observed to have a certain electrical resistance, its temperature may at once be determined by reference to the curve. In order that this process should be practically useful, the following conditions must be complied with.

It is necessary to choose a wire of a material that will not be injured by exposure to high temperatures.

The accuracy with which measurements of temperature can be made by measuring the resistance of a wire will depend on the wire always possessing the same electrical resistance at any particular temperature.

If a very large number of points on the calibration curve need to be obtained experimentally, the preliminary work in calibrating the wire will be much increased. If, on the other hand, it can be proved that the relation between temperature and resistance can be expressed by some simple and well known curve, it may only be necessary to determine a limited number of points through which the curve may be drawn by geometrical or other simple means, thus permitting of a great reduction in the work of calibration.

Sir W. Siemens was the first to attempt to construct a platinum resistance thermometer. It consisted of a platinum wire wound round a fire-clay cylinder, the whole being protected by a stout wrought iron tube. It was found, however, that after having been exposed to high temperatures, the resistance of the platinum wire did not return to its initial value. As a matter of fact, it appears that the silica in the fire-clay cylinder attacked the platinum wire, and thus altered its qualities.

Lately, Prof. Callendar has taken up the question, with the result that he finds that if a coil of pure annealed platinum wire be wound on a mica framework, and thoroughly protected from the action of injurious gases by means of a hard glass or porcelain tube (the choice between these substances being determined by the highest temperature to which the completed thermometer is to be raised), then the temperature as deduced from an observation of the resistance of the wire will seldom be in error by more than about $\frac{1}{100}$° C. The value of this discovery may be understood when it is considered that, even with the application of the corrections previously discussed (See Chap. II.) it is exceeding difficult, with a mercury thermometer, to determine a temperature near 200° C., with no greater error than $\frac{1}{10}$ degree; yet, by the aid of a platinum resistance thermometer, a temperature up to 500° C. may be directly determined with no greater error than $\frac{1}{100}$° C. Even up to 1,300° C., a temperature may be directly determined to within $\frac{1}{10}$°. Thus, in addition to the far wider range afforded by a platinum resistance thermometer, zero errors and a whole host of troublesome corrections are entirely done away with.

Experiment shows that if R_0 is the resistance of a piece of pure platinum wire at 0° C., then the resistance at t° C. may be expressed as

$$R_t = R_0(1 + at + bt^2).$$

This is an equation including three constants, R_0, a, and b; the value of these can be calculated if the resistance of the wire at any three sufficiently remote temperatures is determined. The freezing and boiling points of water afford two convenient temperatures, and the temperature of sulphur boiling under standard pressure was originally used to determine the third point. Sulphur boils at 444·53° C. under standard pressure; if the pressure differs from the standard pressure, 0·082° C. must be added for each extra mm. of mercury.

It has since, however, been shown by Professors Dewar and Fleming that the resistances of pure metals, including platinum, decrease as − 273° C. is approached, thus leading to the conclusion that at − 273° C. the resistance of a pure metal would be zero.[1] It has been found that, by the use of this relation, together with observations of the resistance at the freezing and boiling points of water, a platinum wire may be calibrated with sufficient accuracy for all ordinary purposes.

It will be noticed that the relation between R_t and t may be expressed by a particular parabolic curve. The general form of this curve may be seen by referring to Fig. 175. The complete curve for a particular wire may be quickly plotted by means of a continuous line by joining a number of points, calculated for various values of t from the equation already given.

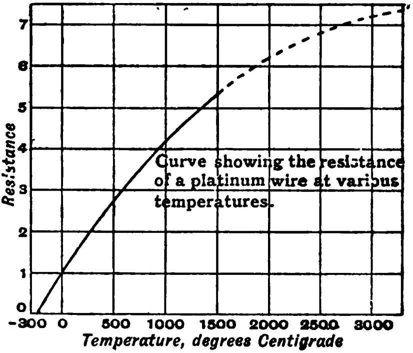

FIG. 175.

Callendar's method of using a platinum resistance thermometer is as follows: The thermometer is supplied with two exactly similar sets of leads, one set T (Fig. 176), being connected to the ends of the spiral of fine platinum wire X, while the other set C (called the *compensating leads*) are joined at their ends within the containing tube of the thermometer. The Wheatstone's bridge arrangement comprises two equal conjugate arms P and Q. Of the other two arms, one comprises the platinum spiral X, the leads T connected across the terminals A B, and the right-hand part of a stretched wire F B;

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[1] More accurate results can be obtained by assuming that the electrical resistance of platinum becomes equal to zero at − 240° C. (Callendar, *Phil. Mag.*, Feb. 1899, p. 218.)

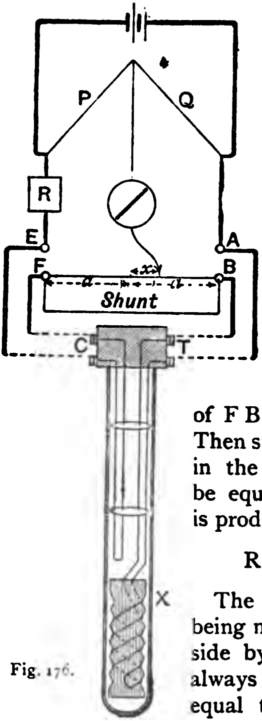

Fig. 176.

the other arm comprises a set of resistance coils R, the compensating leads C connected across E F, and the left-hand part of the wire F B (compare Fig. 176 with Fig. 174). Let X represent the resistance of the platinum spiral, R that of the resistance coils, C and T the resistances of the two sets of leads, and $2a$ the resistance of the wire F B, while x is the resistance of that part of this wire between its middle point and the galvanometer connection, so that the two parts of F B have resistances $(a + x)$ and $(a - x)$. Then since P and Q are equal, the resistances in the other two arms of the bridge must be equal when no galvanometer deflection is produced; in these circumstances

$$R + C + a + x = X + T + a - x.$$

The two sets of leads are exactly similar, being made of the same material and lying side by side, so that their temperatures are always equal, and therefore C is always equal to T. Thus $X = R + 2x$.

EXPT. 65.—**To Construct and Calibrate a Platinum Resistance Thermometer.**—Select a thin-walled test-tube about 12 cm. in length, with an internal diameter of about 1 cm. Cut a rectangular strip of mica about 12 cm. in length, and of a breadth very slightly less than the internal diameter of the test-tube, so that it will just fit into the centre of the latter and be maintained steady there. Scratch fine lines, at intervals of 2 mm., across this strip of mica for a space of about 6 cm. from one end. Small V-notches must now be cut at the ends of each of these lines (Fig. 177). Make four holes through the mica, as shown in the figure, driving a needle of a suitable size through it by a tap from a hammer. These holes are to hold the ends of the leads in position.

Take two pieces of copper wire, about ·75 mm. in diameter, and solder an end of each of two pieces of very fine platinum wire on to one end of each of these. Care must be exercised in effecting the soldering, for at a sufficiently high temperature platinum forms an alloy with lead. The best way of proceeding is to wind one end of the fine platinum wire round the copper, and having slightly wetted the junction with zinc chloride, heat the copper wire half an inch or so *below* the place where the platinum wire is wound, touching the junction of the wires from time to time with a small piece of soft solder. The moment the latter melts heating should be discontinued. If the copper wire is clean, and if enough zinc chloride has been applied, the solder will at once make a good junction between the platinum and the copper. The joint must directly afterwards be well washed with hot water to remove any remaining trace of the zinc chloride.

The free ends of the copper wires are now threaded through the holes in the mica (*see* Fig. 177), the platinum wires being left hanging one on either side of the mica. A cork which fits the test-tube has a channel cut out on its side, so that air can escape from the test-tube when the latter is heated. A cut is made in this cork to take the upper end of the mica slip, and the free ends of the copper wires are threaded through two small holes bored for that purpose. The mica slip will now be firmly attached to the cork. Now commence winding the platinum wire attached to the lead C (say); this follows the course C *a b c d* . . . and *e f*, and is finally passed through a small hole, *g*, at the lower end of the mica. The remaining platinum wire is now wound parallel to the first in the remaining notches, and its end is finally twisted up with the wire projecting from *g*, and the junction soldered by the aid of a soldering bit. The whole may now be enclosed in the test-tube, and the neighbouring ends of a twin flexible cable (such as used for suspending electric glow lamps) can be soldered on to the wires A, B.

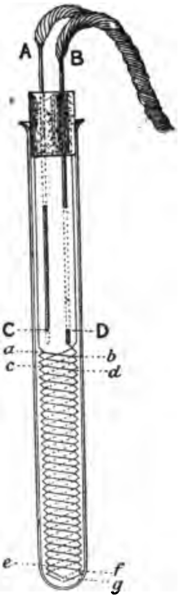

FIG. 177. — Platinum resistance thermometer.

To calibrate this thermometer its resistance is measured when the test-tube is buried almost up to the cork in ice shavings. Make several measurements of the resistance, repeating these till the results obtained reach a constant value.

Be very careful never to depress the battery key for a longer time than is absolutely necessary, otherwise the thin platinum wire will be heated by the current passing through it.

The boiling point is determined by immersing the test-tube in steam, an apparatus similar to that described in p. 11 being used.

The constants in the equation connecting R_t and t can now be calculated, and the curve drawn.

With such a thermometer, much more accurate results can be obtained than with an expensive mercury thermometer.

Advantages of Platinum Resistance Thermometers.—1. Its zero is constant, and a single determination of its resistance at the boiling and freezing points of water will suffice for the plotting of a resistance-temperature curve which will be permanently useful. On the other hand, mercury thermometers require to have their fixed points redetermined at intervals.

2. Readings are quickly taken, and no corrections (such as those for exposed stem, internal and external pressures, &c., which must be used with a mercury thermometer) are in this case required.

3. It possesses a far wider range than any other form of thermometer, except an air thermometer.

4. The magnitude of a platinum resistance thermometer need not be excessive; its tube need not be larger than the bulb of a mercury thermometer of equal sensitiveness.

5. Pure platinum wire, drawn down very fine so as to be suitable for the manufacture of resistance thermometers, can be obtained at a comparatively small cost.[1]

The Bolometer.—The alteration which occurs in the electrical resistance of a platinum wire when the latter is heated, has been utilised by Prof. Langley in the construction of an instrument which he has named the Bolometer, or actinic balance. This instrument is designed to measure the heat produced by the absorption of light (or, more generally speaking, radiation) corresponding to various parts of the spectrum. The instrument itself consists of a couple of gratings, such as indicated in Fig. 178, punched from very thin platinum foil, and covered with a layer of platinum black. The thickness of the foil used only amounted to $\frac{1}{500}$ mm. These gratings form two arms of a Wheatstone's bridge, and the resistances in the remaining arms are so adjusted that, when both gratings are shielded from radiation, the galvanometer needle is

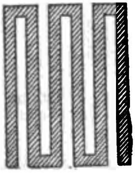

FIG. 178.—Grid for bolometer.

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[1] The very fine platinum wire supplied by Messrs. Johnson and Matthey, of Hatton Garden, London, may be recommended.

undeflected. When radiation is allowed to fall on one of the gratings, its resistance instantly increases and a consequent deflection of the galvanometer occurs. A difference of temperature amounting to $\frac{1}{10000}^\circ$ C. will produce a readable deflection.

Using this instrument, Prof. Langley was able to investigate the heat which reaches us from the moon.

Thermo-Couples.—Let ABC, ADC (Fig. 179) be two pieces of wire of different materials, fused or soldered together at A and C; then if the junction A is maintained at a higher temperature than that at C, an electric current will be generated which may flow round the circuit in either direction according to the materials used, and also according to the difference in temperature between A and C. The two wires are said to constitute a thermo-couple.

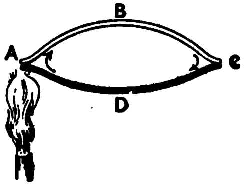

FIG. 179.—Copper-iron thermo couple.

Let us suppose that ADC, ABC (Fig. 179) are two pieces of copper and iron wire respectively. Then, if A is maintained at a temperature 100° C. and C at 0° C., an electric current will flow, at the hotter junction, A, from copper to iron, *i.e.* in the direction of the arrow (Fig. 179). If, however, the mean temperature of A and C is raised to 280° C., there will be no current produced in the circuit; whilst if the mean temperature of A and C is raised still further, a current will flow round the circuit, passing from the iron to the copper at the hot junction, *i.e.* in the direction opposite to that indicated by the arrow (Fig. 179). Most pairs of pure metals exhibit this *thermoelectric inversion*, as it is termed, for certain differences of temperature between the two junctions. Hence, for measurements of very high or very low temperatures, a thermo-couple comprising two wires, one of which is composed of a pure metal and the other of an alloy of that with some other metal of similar properties, is generally used. For high temperature work, it is further necessary that both the metal and the alloy should be infusible.

The Roberts-Austen Recording Pyrometer.—The way in which a thermo-couple may be employed for high temperature experiments is well illustrated by Sir William Roberts-Austen's recording pyrometer, used at the Royal Mint. The wires used are respectively composed of pure platinum and platinum alloyed with 10 per cent. of rhodium. The wire ACB (Fig. 180), composed of the alloy, is fused on to pure platinum wires, ADE and BF, at A and B. The junction A is protected by a fire-clay tube, and is placed in a crucible containing molten metal ; the junction B, which must be maintained at a constant temperature, is surrounded by steam in a vessel similar to that used for obtaining the boiling point of a thermometer. The two free ends of the platinum wires, ADE and BF, are connected to the terminals of a sensitive snspended coil galvanometer, G. It is arranged that the resistance of this instrument is so great that any variation in the electrical resistance of the wires composing the thermo-couple will not produce any appreciable effect on the current generated. Consequently, a definite deflection of the galvanometer G will correspond to a definite temperature of the junction A.

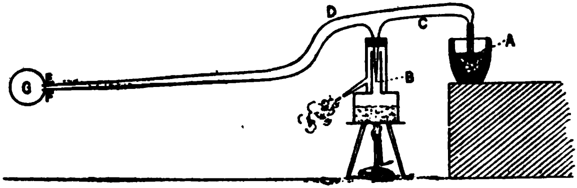

FIG. 180.—The Roberts-Austen recording pyrometer.

The above arrangement was designed to obtain a cooling curve for solidifying metals and alloys, *i.e.* to determine how the temperature of a metal or alloy varies as it passes from a molten to a solid state. In order to do this, an arrangement for obtaining a photographic record of the galvanometer deflection is employed. The needle of the galvanometer is provided with a small silvered mirror, from which a ray of light is reflected on to the photographic plate. As the needle is capable of twisting only about a vertical axis, if the photographic plate is kept stationary, and the galvanometer deflection varied continuously, a horizontal line will be found on the plate after development. On the other hand, if the galvanometer needle remains in its zero position whilst the photographic plate is gradually raised or lowered, a vertical line will be found on the plate after development. The line OO (Fig. 181) is such a zero line; all points on this line will correspond to equality of temperature between A and C, *i.e.* to a temperature of 100° C. at the thermo-junction A. In order to lower the photographic plate slowly and continuously, it is supported on a float which is partly immersed in water contained in a vessel. If this water is

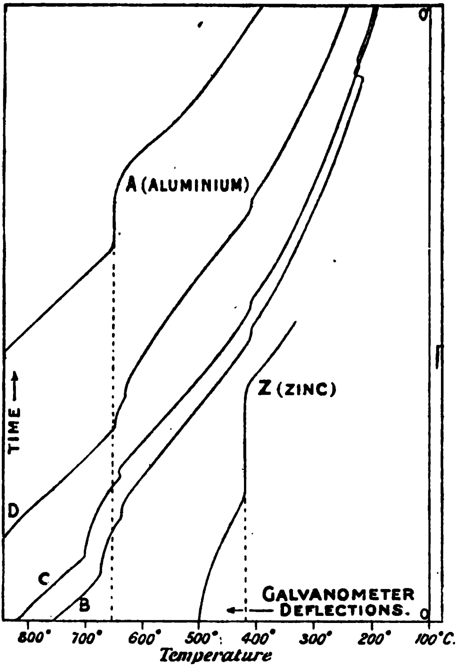

FIG. 181.—Curves obtained by the Roberts-Austen recording pyrometer.

drawn off uniformly by the aid of a tap, the desired movement will be attained.

Let us suppose, now, that pure molten aluminium is placed in the crucible, thus surrounding the junction A. A deflection of the galvanometer is produced, which will decrease as the temperature of the aluminium falls. Consequently, we find the temperature variation of the aluminium represented at first by an inclined straight line, due to the gradual motion of the spot of light to the right, combined with the downward motion of the plate. After a short time, the curve changes into a vertical straight line; this denotes that the temperature has remained constant for a certain period. Afterwards, the galvanometer needle has again moved toward the right, indicating a further fall of temperature.

As already explained (*see* Chap. VIII., p. 164) the temperature corresponding to the vertical portion of the aluminium curve is the *melting point* of aluminium. The curve Z is obtained on the same plate by repeating the above procedure, using zinc instead of aluminium in the crucible. We have now obtained the galvanometer deflection corresponding to 100° C. (zero line), 660° C. (melting point of aluminium), and 420° C. (melting point of zinc). We can consequently construct the temperature scale given at the bottom of the figure.

The curves B, C, and D, were obtained immediately after A and Z on the same plate. They correspond to alloys of copper and tin, containing respectively 50, 55, and 45 per cent. of copper. At some points it will be noticed that these curves denote a constant temperature for a small interval of time; at other points, a slight increase in temperature is seen to have occurred. These points, which could not have been observed by the aid of an ordinary thermometer, are of the greatest importance in studying the properties of alloys.

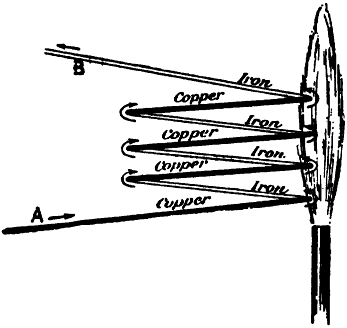

FIG. 182.—Simple form of thermopile.

The Thermopile.—If a number of copper and iron wires are joined together as indicated in Fig. 182, the free ends, AB, being connected to a galvanometer, a comparatively strong current will pass through the latter when one set of junctions is heated as shown. If the wires are thick, and the electrical resistance of the galvanometer is high, for a given difference of temperature between the hot and cold junctions, the deflection of the galvanometer will be proportional to the number of couples employed.

An arrangement such as that described is termed a thermopile. As a general rule, antimony and bismuth are used instead of iron and copper.

In order to diminish the electric resistance which the current will experience in passing through the thermopile, small rectangular rods are used.

A thermopile consisting of 18 couples is represented in Fig. 183. The bismuth bars are shaded, the antimony bars being left clear. The thick lines indicate the position of insulating material, such as mica, whilst the fine lines indicate the soldered unions of the bismuth and antimony bars.

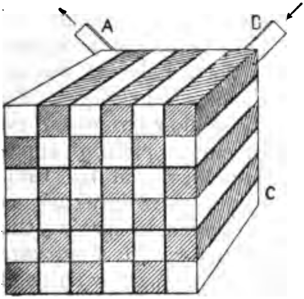

FIG. 183.—Thermopile.

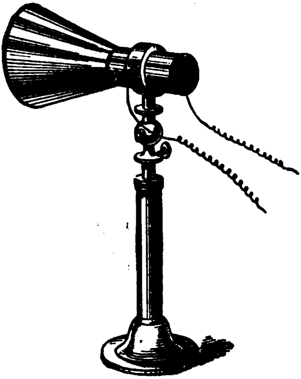

FIG. 184.—Thermopile mounted ready for use.

When the near face is heated, a current will flow across the hot junctions from bismuth to antimony. The current will enter the pile at B, and flow downward in a zigzag direction through the right hand layer of couples. On reaching C, the current enters the lowest bismuth bar in the next layer, and then flows up that layer. On finally reaching the terminal A, the current leaves the pile.

A thermopile mounted ready for use is represented in Fig. 184. Its exposed faces are blackened so as to readily absorb radiant energy; they can be covered with brass caps when it is wished to screen them from radiation. A metal cover is generally mounted at the exposed end of the pile during experiments on radiation; by this means, the exposed face is protected from air currents, and from radiation proceeding from bodies other than that of which the radiating power is being investigated.

The Radio-Micrometer.—Since a large mass of metal is used in the construction of a thermopile, a considerable amount of heat must be absorbed before any appreciable change of temperature is produced in the metal near one of the exposed surfaces. In the radio-micrometer, an ingenious piece of apparatus invented by Prof. Boys, this drawback is overcome, by making the thermo-couple from very thin and narrow strips of antimony and bismuth, connected at one end by means of a very thin piece of blackened copper foil. The other ends of the bismuth and antimony strips are connected to the extremities of a long narrow coil of a single turn of wire (Fig. 185). This coil is suspended by a quartz fibre, so that it hangs between the poles of a powerful electromagnet. When no current passes through the coil, the quartz fibre constrains it to hang with its plane parallel to the line joining the magnet poles. When any radiation falls on the piece of blackened copper foil, this latter is heated, and a current flows round the suspended circuit. As the rotation of this circuit is only

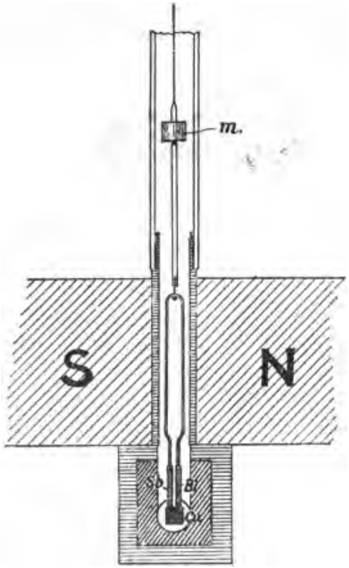

FIG. 185.—Professor Boys's radio-micrometer.

opposed by the feeble torsional force of the quartz fibre, a very small current produces a considerable rotation, the magnitude of which can be measured by the aid of a beam of light reflected from a very small silvered mirror, *m*, attached to a piece of thin capillary glass tubing, which connects the coil with the quartz fibre.

It will be seen that the radio-micrometer is really a combination of a thermo-couple with a very delicate suspended coil galvanometer. By means of this instrument, the heat communicated to us by radiation from the moon can be accurately measured. Valuable information has also been afforded by its use in respect of other astronomical bodies. For instance, from the fact that the planet Jupiter is enveloped in great masses of cloud, it had been assumed that the temperature of that planet was very high. Prof. Boys assured himself that if the temperature of Jupiter were as high as 100° C., the heat radiated from it could be detected by the aid of the radio-micrometer. As no deflection was produced when the image of Jupiter, formed in a reflecting telescope, was thrown on the small blackened copper disc of the radio-micrometer, the conclusion reached was that Jupiter was at a lower temperature than 100° C.

The heat communicated to us by radiation from the stars could not be detected by the aid of the radio-micrometer.

SUMMARY OF CHAPTER XIX.

A Galvanometer is an instrument designed to measure or detect the presence of electrical currents. In some cases a suspended magnet is deflected by the action of the electric current circulating in fixed coils, whilst in others a suspended coil is deflected by the action on fixed magnets of the current which flows through it.

Platinum Resistance Thermometer.—The electrical resistance of pure platinum would apparently be equal to zero, at the absolute zero of temperature, and varies with the temperature of the platinum. Consequently a measurement of the resistance of a piece of platinum wire may be used to determine the temperature of the wire.

Thermo-couples.—If a closed circuit is formed of two different metals, and one of the junctions is heated, an electric current will flow round the circuit. For a given circuit, the current produced will depend on the difference of temperature between the hot and cold junctions. This gives a means of measuring very high or very low temperatures.

A Thermopile consists of a number of thermo-couples arranged in such a manner that all the couples tend to produce an electric current flowing in one direction round the compound circuit.

Prof. Boys's Radio-Micrometer is a combination of a very light thermo-couple with a delicate suspended coil galvanometer.

QUESTIONS ON CHAPTER XIX.

(1) Describe fully the arrangements you would make in order to compare the scales of the electrical resistance thermometer, and of the air thermometer.

(2) Give a critical account of methods which have been devised for the measurement of very high temperatures.

(3) Describe the radio-micrometer of Prof. Boys.

(4) Describe and explain the principles of the action of the thermopile.

(5) Describe a method of measuring a high temperature, such as that of a furnace.

(6) Describe some form of electrical pyrometer.

(7) Describe some instruments practically used in the measurement of very high temperatures.

CHAPTER XX

CONVECTION AND CONDUCTION OF HEAT

Convection of Heat.—When a fluid is heated, as a general rule its density is diminished. If only a part of a fluid is heated, the difference of density thus produced may cause currents to be set up. The action of these currents will be to carry the warm fluid away from the point at which heat is being communicated, whilst its place is taken by colder fluid from surrounding parts. Hence the tendency is to equalise the temperatures throughout the fluid. Since heat is *conveyed* from place to place by finite portions of the fluid, the process is termed *convection* of heat.

EXPT. 66.—Take a round-bottomed glass flask, partly fill this with water, and drop a few crystals of magenta into it. Heat the flask by means of a very small Bunsen flame. As the water passes the crystals of magenta it becomes coloured. Its subsequent path is indicated by coloured streaks in the water (Fig. 186). It is thus seen that the heated water rises through the centre of the flask; after being cooled by contact with the cold water in the upper parts of the flask, it descends near the walls of the latter, and finally gets heated once more. After a short time the water throughout the flask will become uniformly coloured, thus showing how well the water is mixed by means of the convection currents produced.

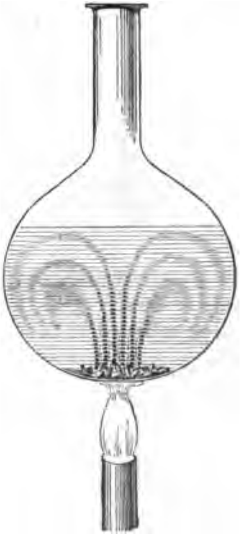

FIG. 186.—Arrangement for showing the convection of heat in water.

In the above experiment, the heated water rises through its colder surroundings by virtue of its diminished density; just as a drop of paraffin oil, which is less dense than water, will rise through the latter.

EXPT. 67.—Take a glass tube, of the form shown in Fig. 187; fill this with water, and drop a few crystals of magenta through the open neck. Now heat one of the vertical side tubes by means of a spirit lamp or Bunsen flame. The path of the convection currents set up will be indicated by lines of coloured water (*see* Fig. 187).

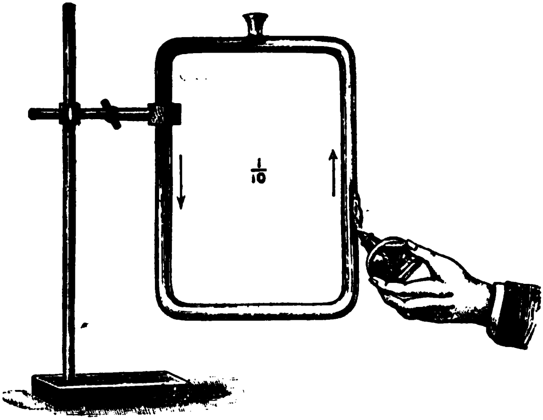

FIG. 187.—Convection of heat in water.

EXPT. 68.—Make a small paper box by folding writing paper (Fig. 188). The flaps may be stuck down by means of sealing wax. Suspend this box by means of fine wires, and half fill it with water. It will be found that this water can be boiled by the aid of a Bunsen flame, whilst the paper will not be scorched where it is in contact with the enclosed water. This shows that the water conveys the heat away from the paper as quickly as it is communicated.

Joule's Determination of the Temperature of Maximum Density of Water.—In this experiment two long metal cylinders, similar to those shown in Fig. 189, were employed. The cylinders were placed vertically, and communication was established near their upper ends by means of a shallow trough, whilst a tube provided with a stop-cock served when required to establish communication between their lower extremities. Both cylinders were filled with water, and the stop-cock being closed, the water in one cylinder was cooled by the addition of ice shavings. After the water in each cylinder had been well stirred, the stop-cock was opened. If there was any difference in density between the water in the two cylinders, convection currents, similar to those made evident in Expt. 67, were produced. These currents were indicated by the motion of a small float placed in the trough connecting the upper ends of the cylinders. By trial it was finally found that the density of water was the same at two different temperatures, one above and the other below 4° C. (Cf. Fig. 42). By performing this experiment with the warmer water at a number of different temperatures approaching 4° C., the temperature of maximum density was at last found.

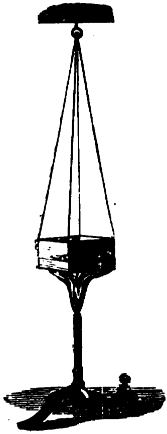

FIG. 188.—Water boiled in a paper vessel.

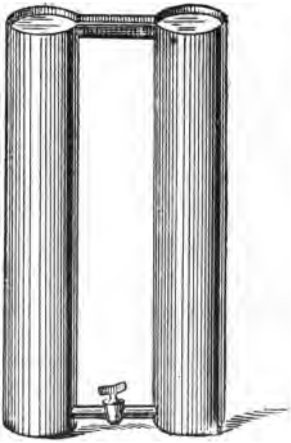

FIG. 189.—Joule's method of determining the temperature corresponding to the maximum density of water.

Winds.—When the air near one part of the earth's surface is heated, this air rises, and air from other colder parts of the atmosphere rushes in to take its place. Thus winds are produced. The direction of motion of the air is often affected by the motion of the earth.

Land and Sea Breezes.—During the day, whilst heat is being communicated by the sun, the temperature of the land rises more quickly than that of the sea. This is partly due to the exceptionally high specific heat of water. The communication of a given quantity of heat will raise the temperature of a pound of sand, rock, or soil, to a much greater extent than a pound of water. The earth communicates part of its heat to the surrounding air, and this air rises, whilst colder air from over the sea rushes in to take its place. This constitutes a *sea breeze*, which blows during the day.

During the night the earth cools more rapidly than the sea, for the reason discussed above. (Compare this result with the method of determining the specific heat of a substance by cooling, p. 129.) Hence, shortly after sunset the sea is warmer than the land. Consequently, air currents flow from the land to take the place of the hot air which rises from over the sea. These currents constitute *land breezes*.

Ocean Currents.—Currents flow from warm to colder parts of the ocean, for reasons similar to those discussed in connection with Expt. 66. The directions of these currents are modified by the motion of the earth, and the configuration of the land.[1]

Conduction of Heat.—*When heat is propagated from one part of a body to another, without the occurrence of motion in any finite part or parts of the body, intermediate points being heated meanwhile, the process of transfer is termed conduction.*

The most familiar instances of conduction are furnished by solid metallic bodies.

EXPT. 69.—Take similar rods of copper and iron, and place an end of each in the fire. After a short time it will be found that the free end of the copper rod is too hot to be held in the hand, whilst the corresponding end of the iron rod is still hardly warmer than at first.

In the case of the copper, heat has been directly communicated to the end of the rod which is in the fire, and this heat has travelled along it without the occurrence of any motion of finite parts of the rod. Hence, heat has been transmitted by conduction.

In the case of the iron rod, a similar transference has occurred, though to a much smaller extent.

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[1] For a full description of the air and ocean currents of the earth, the student is referred to Simmons's *Physiography*. (Macmillan & Co.)

All bodies conduct heat, though some to a much smaller extent than others. As a general rule, substances which, like silver and copper, are good conductors of electricity, will also conduct heat readily. Iron and lead, which are bad conductors of electricity, are also bad conductors of heat. Glass (which is, comparatively speaking, a non-conductor of electricity) conducts heat very badly indeed. Thus it is possible to fuse one end of a glass rod, and raise it to a bright white heat, whilst the glass an inch or so up the tube remains quite cool.

There are, however, no substances known which are total non-conductors of heat.

EXPT. 70.—*To illustrate the difference in the conductivities of wood and brass.*—Take a flat piece of wood, and form a pattern on its surface by the insertion of ordinary brass wood-screws. File the heads of the screws down to be flat with the wood, and then rub the common surface on a piece of glass paper placed on a flat board. Paste a piece of *thin* paper (the cheapest foolscap will answer well) over the surface and leave it to dry. Then hold the surface over a Bunsen flame. It will be found that the paper chars over the wood, but remains unburnt where it is in contact with the brass (Fig. 190). The difference in the conductivities of different parts of the grain of the wood will also be made manifest.

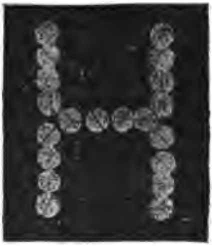

FIG. 190.—Shows paper charred where in contact with wood, but unburnt where in contact with brass.

The paper, when heated, communicates heat to the surface immediately in contact with it. In the case of the brass the heat is conducted to the remote parts of the screws; if the points of the screws project through the wood, these will soon be felt to be hot. On the other hand, wood is a bad conductor of heat, so that very little heat is conducted into the interior of the wood. Hence the temperature of the paper over the wood quickly rises till charring occurs, whilst the paper in contact with the brass remains cool.

It is for similar reasons that, on a frosty day, a piece of metal is colder to the touch than a piece of wood.

The Davy Safety Lamp.—In order that a mixture of air and any inflammable gas should burn, a certain temperature, termed the *temperature of ignition* of the mixture, must be attained. If one end of a copper rod is introduced into a flame, the gases near it will be cooled, and a space surrounding the rod will be seen to remain dark.

EXPT. 71.—Coil a piece of copper wire, of about $\frac{1}{16}$ inch diameter, round a rod of such a size that the coil will just enclose the flame of a spirit lamp. Leave a length of wire for a handle. Light a spirit lamp, and lower the coil axially over the flame.

It will be seen that the alcohol vapour cannot burn inside the coil. When the latter has been lowered sufficiently, the flame goes out.

If, on the other hand, the coil of wire is first raised to a red heat, it will be found that the lamp is no longer extinguished when the coil is lowered over the flame.

The explanation of these experiments is simple. In the first case so much heat was absorbed by the wire, that the mixture of alcohol vapour and air was cooled below its temperature of ignition. In the second case, the wire, being initially hot, did not cool the mixture to the same extent.

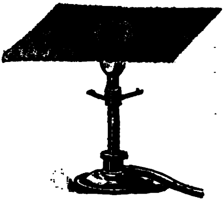

FIG. 191.—Bunsen flame burning below, but not above, wire gauze.

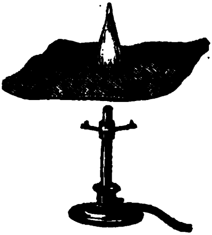

FIG. 192.—Bunsen flame burning above, but not below, wire gauze.

EXPT. 72.—Ignite a Bunsen flame, and bring a piece of wire gauze down in a horizontal position over it (Fig. 191). The gauze will appear to crush the flame down. There will be no flame above the gauze unless the latter becomes very hot, when the unburnt gases above it will ignite.

EXPT. 73.—Place a piece of wire gauze an inch or so above an unignited Bunsen burner. Turn on the gas, and light it above the gauze. It will be seen that the flame does not strike down through the gauze (Fig. 192).

The property possessed by wire gauze, of preventing a flame from passing through it, was utilised by Sir Humphry Davy in constructing a lamp to be used in mines where fire-damp is prevalent. He used an ordinary oil lamp, of which the flame was surrounded by a wire gauze cylinder closed at the top by a metal plate (Fig. 193). Atmospheric air can readily reach the wick of the lamp through the gauze, so that the burning of the lamp is not interfered with. On the other hand, the hot gases produced by the flame are cooled by the gauze, so that if it is placed in an inflammable mixture of gases, these latter cannot be sufficiently heated for ignition to occur. If placed in a mixture of fire-damp and air, these gases penetrate through the gauze and burn inside with a blue flame. The outside gases, however, are not ignited.

If a safety lamp is burning in a chamber filled with fire-damp and air, and a pistol is fired in the immediate neighbourhood, the blue flame is sometimes forced through the gauze, and the external mixture of gases is ignited. The sudden compression of the air, due to the report of the pistol, forces the hot gases through the gauze, without giving them time to part with their heat. This points to a danger in the use of safety lamps such as shown in Fig. 193.

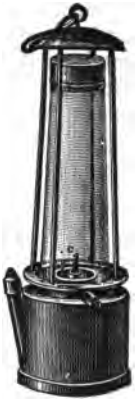

FIG. 193.—Davy safety lamp.

Physical Nature of Conduction.—When part of a substance is heated, the molecules in the neighbourhood of the heated point are thrown into a state of violent agitation. If the substance is a solid, it is impossible for the molecules to move through any great distances. On the other hand, when a molecule moving with great velocity strikes against one moving more slowly, kinetic energy will be transferred from the first to the second molecule. This latter molecule, in its turn, will communicate part of its acquired energy to other molecules; consequently, we have a continual transference of energy from molecule to molecule.

Since heat is the kinetic energy corresponding to the motions of the molecules of a body, we are able to form a clear mental picture of the process by which heat is conducted from place to place by conduction.

It is necessary to remark, that during the conduction of heat from one place to another, all intermediate points are heated. Thus, the molecules do not give up all, but only a part of this newly-acquired kinetic energy.

If a cubical block of metal is taken, and one face is maintained at a higher temperature than the opposite one, heat will pass through the block, and in a given time a definite quantity must be removed from the colder face in order that the temperature of that face may remain constant.

Coefficient of Conductivity of a Substance.—Let us suppose that we are provided with a slab of some substance, very long and broad in comparison with its thickness (Fig. 194). Let us maintain the two opposite faces of the slab at different temperatures. Then heat will flow through the slab in the direction of the arrow (Fig. 194). If we could examine a small centimetre cube, such as that shown in dotted lines, with two of its faces parallel to the faces of the slab, then we should find that heat enters through the face nearest to the high temperature side of the slab, and leaves through the opposite face. Heat will neither enter at, nor leave by, the other faces of the cube, since the flow of heat is parallel to the arrow. When a steady state has been attained, there will be a certain constant difference of temperature between the faces of the cube which are perpendicular to the arrow; consequently in a given time as much heat must pass into the cube through one face as leaves it through the opposite face.

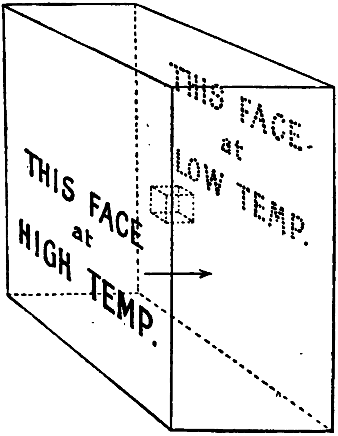

FIG. 194.—Illustrates the method of defining the coefficient of conductivity of a substance.

The quantity of heat which passes through the cube, in one second, divided by the difference in temperature between the faces through which the heat passes, is defined as the **coefficient of conductivity** of the substance.

The meaning of this definition may be made clearer by the aid of a numerical example.

Example.—What is the coefficient of conductivity of a badly conducting substance upon which the following experiment was made? A tin cylinder, 40 cm. in diameter and 50 cm. in length, is covered all over by a layer of the material in question, 0·33 cm. in thickness. Steam is passed through the cylinder at a temperature of 100° C., and the external temperature being 20° C., water is found to accumulate at the rate of 3 grams per minute. The latent heat of steam at 100° C. may be taken as 537 therms per gram. (Lond. Univ. B. Sc. Pass, 1897.)

Area of each end of cylinder $= \pi r^2 = \pi \times (20)^2 = 1{,}256$ sq. cm.
Area of curved walls of cylinder $= 2\pi \times 20 \times 50 = 6{,}280$ sq. cm.

∴ Total area covered with conducting material =

$$6{,}280 + 2 \times 1{,}256 = 8{,}792 \text{ sq. cm.}$$

Since $\frac{3}{60}$ grams of water are condensed per second, the quantity of heat passing in each second through the layer of badly conducting material =

$$\frac{3}{60} \times 537 = \frac{161 \cdot 1}{6} \text{ therms.}$$

∴ Quantity of heat passing per sec. through each sq. cm. of surface =

$$\frac{161 \cdot 1}{6 \times 8{,}792} \text{ therms.}$$

Difference in temperature between opposite sides of a layer of non-conducting material $= 100 - 20 = 80°$ C.

In passing through a layer of the material 0·33 cm. thick, the fall of temperature = 80° C.

∴ Fall of temperature per centimetre $= \frac{80}{\cdot 33}$ °C.

∴ Coefficient of conductivity =

$$\frac{\text{Heat passing through 1 sq. cm. in 1 sec.}}{\text{Fall of temperature per centimetre}} =$$

$$\frac{161 \cdot 1 \times \cdot 33}{6 \times 8{,}792 \times 80} = \cdot 0000126 = 1 \cdot 26 \times 10^{-5}.$$

Determination of the Conductivity of a Metal by Forbes's Method.—If one end of a metal bar is heated, the other end remaining at the temperature of the atmosphere, heat will travel along the bar, and after some time the various points along the bar will have attained steady temperatures. In this case the heat entering the bar at the hot end will be entirely given up to the atmosphere, or radiated into space, from the surface of the bar.

If we consider a part of the bar comprised between two planes perpendicular to its length and one centimetre apart, we may, if the bar is sufficiently long, neglect the heat given off by the surface between the planes, in comparison with that given off by the surface of the bar beyond them. Hence, the sectional area of the bar being known from direct measurement, if we can determine the fall of temperature between the planes, and also the amount of heat given off from the surface of the bar beyond them, the coefficient of conductivity of the metal employed can be calculated from the formula :—

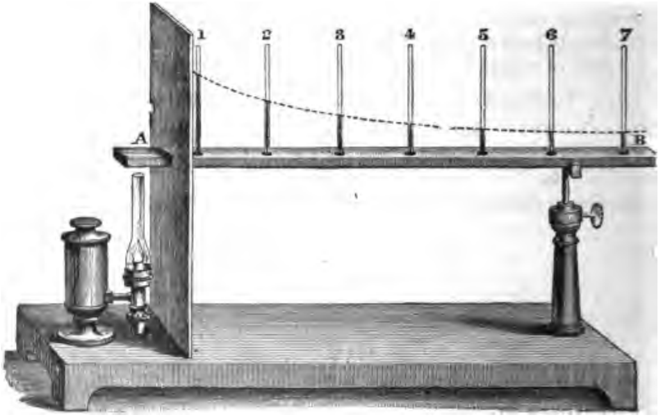

FIG. 195.—Arrangement for measuring the coefficient of conductivity of a metal. (P.)

$$\text{Coefficient of conductivity} = \frac{\text{Heat passing through 1 sq. cm. of sectional area in 1 sec.}}{\text{Fall of temperature per cm. length.}} \quad (1)$$

Forbes made two distinct sets of experiments on each bar, in order to determine the quantities occurring in the above formula.

1. *Statical Experiments.*—In these an arrangement somewhat similar to that represented in Fig. 195 was employed, except that the end of the bar was heated by being inserted into a crucible full of fused solder, which was maintained at a constant temperature. Small holes were made in the upper surface of the bar, and these inclosed thermometer bulbs, surrounded with small quantities of mercury in order to effect a good thermal communication between the bulbs and the metal of the bar. When the thermometers indicated that the various points along the bar had acquired constant temperatures, these latter were noted, and a curve similar to Fig. 196 was drawn, indicating the fall of temperature along the bar. OC represents the length of the bar. If two points A,B, are taken, corresponding to points on the bar one centimetre apart, the fall of temperature per centimetre length at the position in question is given by the line DE.

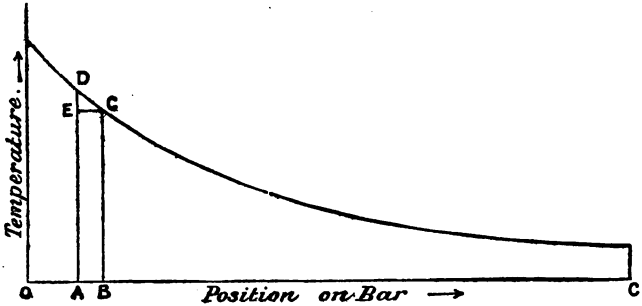

FIG. 196.—Statical curve of temperatures (Forbes's method).

These experiments were termed *statical*, since each point of the bar was allowed to attain a constant temperature before observations were made.

2. *Dynamical Experiments.*—The bar used in the previous experiment was heated uniformly throughout its length, and then supported on knife edges, and the rate of cooling was determined for various temperatures. These experiments were termed dynamical, since the temperature was changing whilst observations were being made.

The quantity of heat given up by the bar, during a given interval of time in which the temperature fell by a certain number of degrees, was calculated from the experimental data, and the relation,

Mass of bar × specific heat × fall of temperature = heat given up by the bar, in given interval of time, when at a known mean temperature.

From this the heat given up by unit length of the bar in one second, for a given mean temperature, was calculated. A new curve, representing the relation between the heat given up by unit length of bar in one second, and various mean temperatures, was drawn.

Now from Fig. 196 the mean temperature of the length BC of the bar can be calculated. The heat given up per second by the length BC for this mean temperature can be obtained by the aid of the curve drawn from the results of the dynamical experiments.

But this quantity of heat has passed through the section of the bar at A. Hence, the area of the section being known, the heat passing through 1 sq. cm. at A can be found. This quantity is the numerator of the fraction on the right-hand side of (1). The denominator, which is numerically equal to the length DE, Fig. 196, has already been obtained. Hence, the coefficient of conductivity of the substance can be calculated.

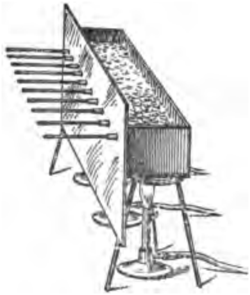

FIG. 197.—Ingen-Hausz's method of comparing conductivities of metal rods.

Comparison of Conductivities. — Ingen-Hausz's Experiment.

EXPT. 74.—You are provided with a trough furnished with apertures in its side, through which a number of rods of different metals can be fixed by means of corks (Fig. 197). The rods are of equal lengths and of equal circular sectional areas. They must first be coated uniformly with layers of paraffin wax. This can be done by dipping each in turn into a bowl of melted paraffin wax, withdrawing it, and rotating till the wax has solidified. Then fix the rods in position, fill the trough with water, and support it on tripod stands. Heat the water by the aid of Bunsen burners, a sheet of asbestos card being placed as shown in Fig. 197, so as to prevent the heat of the flames from reaching the rods. Observe the distance from the trough to which the paraffin is melted off each rod when the water has been boiling for about a quarter of an hour.

The ends of the rods which are inserted into the trough are all at the temperature of boiling water. At the points farthest from the trough where the wax is just melted, the temperature is that of melting wax, *i.e.*, 52° C. Hence, the mean temperatures of those parts of the rods from which the wax is melted are equal. Therefore, if the surfaces of the rods are uniform, the amount of heat given off per second from the part from which the wax is melted will be proportional to the distance to which the wax is melted.

Let l be the distance, along any particular rod, through which the wax is melted.

Then, quantity of heat given off per second from that length of rod $= kl$, where k is a constant for all the rods . . . . . (*a*)

This quantity of heat represents the excess of the heat entering the rod at the hot end, over that which passes across the section where the wax is just melted, toward the cold end of the rod, in one second.

Now, the heat passing per second through any section of the rod will be proportional to the fall of temperature per centimetre length at the given section, multiplied by the conductivity of the substance of which the rod is composed. (*Cf.* p. 420.)

Since in all cases the temperature falls from 100° C. to 52° C. in passing along a rod through the distance l, the fall of temperature per centimetre length at points possessing equal temperatures on various rods will be inversely proportional to l.

Therefore, we may write,

$$\left.\begin{array}{ll}\text{Heat entering hot end of rod per second} \; . \; . \; . \; . & = \dfrac{C\kappa_1}{l} \\ \text{Heat passing through section of rod where wax} & \\ \quad \text{is just melted, per second} \; . \; . \; . \; . \; . \; . \; . \; . \; . & = \dfrac{C\kappa_2}{l}\end{array}\right\} (b)$$

where C = conductivity of substance composing rod, κ_1 and κ_2 are constants, depending only on the temperatures, viz., 100° C. and 52° C., at the two points in question.

$\therefore$ from (*a*) and (*b*),

$$kl \propto \left(\frac{C\kappa_1}{l} - \frac{C\kappa_2}{l}\right)$$

$$\therefore kl \propto \frac{C}{l}(\kappa_1 - \kappa_2)$$

$$\therefore C \propto \frac{k}{\kappa_1 - \kappa_2} l^2 .$$

Since k, κ_1 and κ_2 are constant for all the rods, we see that the *conductivity* C *of any rod will be proportional to the square of the distance through which the wax has been melted.*

Relative conductivities can also be determined by placing similar bars of two substances end to end, small bullets being attached to their lower surfaces by means of beeswax at equidistant points. If the junction of the two bars is now heated and maintained at a constant temperature, the relative conductivity of either bar will be proportional to the square of the number of bullets which finally have fallen from it.

Most lecture experiments on the conductivities of metals occupy too much time to be very effective, and in addition are often somewhat uncertain in their action. The following arrangement[1] may be very quickly and simply put together, and by its aid the relative conductivities of a number of metals may be quantitatively determined in an interval of about a minute, the essential parts of the apparatus being capable of projection on a screen. It can also be used in the laboratory.

EXPT. 75.—A piece of brass tube, about 10 cms. in diameter and 20 cms. in length, is closed at one end by means of a brass disc. A number of holes are bored in this disc to receive rods of copper, brass, iron, &c., each rod being 2·5 mm. in diameter and about 15 to 20 cms. in length. The rods are soldered in position perpendicular to the disc.

Each rod is provided with a small index made from a piece of copper wire of about ·8 mm. diameter, bent into the form shown in Fig. 199, a small arrow-head of blackened paper or mica being attached by shellac varnish. The rings forming part of each index are wound on a rod *very slightly* larger in diameter than the experimental rods.

To start with, the brass vessel is inverted, an index is slipped on each rod, the single ring (Fig. 199) being left in contact with the disc, and a very small amount of paraffin wax is melted round the rings. When the vessel is supported with the rods downwards, as in Fig. 198, the solid wax holds the indexes in position. The arrangement is then supported between the condenser and the focussing lens of the lantern, and boiling water is poured into the brass vessel. When that part of a metal rod in the neighbourhood of the double ring of the index reaches the melting temperature of the wax, the index commences to slip downwards, carrying the wax with it, and when the temperatures of the rods have acquired steady values, the indexes will have descended to points on the various rods where the wax just solidifies, and which, therefore, possess equal temperatures. Hence the conductivities of the various rods are proportional to the squares of the distances from the bottom of the brass vessel to the positions indicated by the several arrow-heads.

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[1] "A Lecture Experiment on the Relative Thermal Conductivities of Various Metals."—Edwin Edser, *Nature*, July 13, 1899.

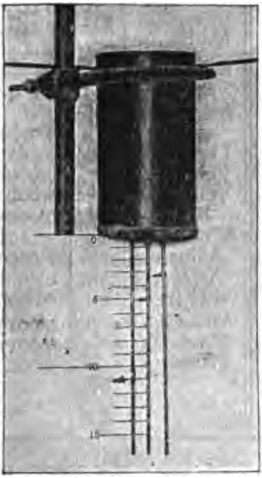

FIG. 198.—Arrangement for determining the relative thermal conductivities of metal rods. (The left-hand rod is of copper, the middle one of brass, and the right-hand one of soft steel.)

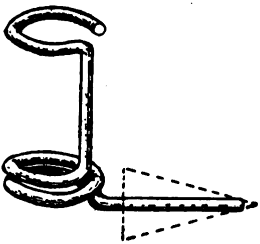

FIG. 199.—Enlarged view of index.

A scale of equal parts, or better still, a scale of squares, may be drawn on the screen, when the relative conductivities may be directly read off.

In Fig. 198, rods of copper, brass, and soft steel are shown with the indexes in the positions acquired at the end of an experiment. It will be seen that the relative conductivities work out to within three or four per cent. of the accepted values for the mean conductivities between 0° and 100°.

TABLE OF HEAT CONDUCTIVITIES OF VARIOUS SUBSTANCES.

Substance.	Mean Temperature.	Coefficient of Conductivity.	Substance.	Coefficient of Conductivity.
Aluminium	0°	0·343	Clay Slate	0·00272
	100°	0·362	Granite from	0·00510
Antimony	0°	0·0442	Granite to	0·00550
	100°	0·0396	Marble from	0·00470
Bismuth	0°	0·0177	Marble to	0·00560
	100°	0·0164	Sand (white, dry)	0·00093
Brass (yellow)	0°	0·2041	Serpentine	0·00441
	100°	0·2540	Snow, in compact layers	0·00051
Cadmium	0°	0·220		
	100°	0·245	Plaster of Paris	0·0013
Copper	0°	0·7189	Pasteboard	0·00045
	100°	0·7226	Vulcanised Rubber from	0·00034
Iron	0°	0·166	Vulcanised Rubber to	0·00054
	100°	0·163	Wood, Fir—	
Lead	0°	0·0836	Along the grain	0·0003
	100°	0·0764	Across the grain	0·00009
Mercury	0°	0·0148	Wax (bees')	0·00009
	50°	0·0189	Water	0·00136
Silver	0°	0·960	Glass	0·0017
Tin	0°	0·1528	Flannel	0·00003
	100°	0·1423		
Zinc	0°	0·303		

From the above table it is seen that the conductivity of a metal varies with the temperature. Thus, if a slab of copper 1 cm. thick is maintained with one face at 101° C., and the other at 100° C., 0·7226 therms will be transmitted in a second through each square centimetre of area. On the other hand, if the temperatures of the faces are maintained at 1° C. and 0° C. respectively, 0·7189 therms will be transmitted in a second through each square centimetre of area.

Temperature Waves.—If a slab of metal, initially at a uniform temperature throughout, has the temperature of one of its faces suddenly raised, a wave of increasing temperature will travel through the slab. The rate at which this temperature wave travels is no measure of the conductivity of the substance. In order to determine the latter quantity, the specific heat of the substance must be known, so that the quantity of heat which travels through a given area in a certain time may be calculated. Thus Prof. Tyndall showed that a temperature wave travels faster in bismuth than in iron, although the conductivity of iron is nearly ten times as great as that of bismuth.

The rate at which a temperature wave travels in a substance is a measure of what has been termed the *diffusivity of temperature* (Kelvin), or the *thermometric conductivity* (Maxwell) of the substance.

Terrestrial Phenomena and the Age of the Earth.—During the daytime the surface of the earth is heated, and a wave of temperature travels into the interior. These diurnal waves only reach, on an average, to a depth of about 3 feet. The mean temperature of the surface of the earth is higher in summer than in winter. Consequently, annual waves of temperature also travel into the interior of the earth.

The rate at which these waves travel has been determined from observations of the annual and diurnal variations of temperature at different depths in borings. From these, combined with a knowledge of the mean specific heat of the earth's crust, Lord Kelvin has calculated the heat conductivity of the latter.

In descending to great depths into the interior of the earth, the temperature steadily rises by about 1° C. for every 108 feet of descent. Hence heat must be steadily travelling from the interior to the surface of the earth. From the rate at which heat is at present being lost by the earth, Lord Kelvin estimates that 200,000,000 years have elapsed since the earth was in a molten condition, with a thin solid crust.

The fact that the interior of the earth is still very hot, does not prove that there is still a molten core. Most of the substances composing the earth's crust contract on solidifying. Hence, the enormous pressure near the centre of the earth may suffice to maintain them in a solid condition (pp. 177 and 372).

Conductivity of Crystals.—Many crystals are *æolotropic* (p. 60) as regards heat conductivity. Thus, the conductivity of such a crystal will depend on the direction of transmission of heat. Fig. 200 represents the method used by M. de Senarmont to determine the relative conductivities in various directions in a crystal. A thin plate of the crystal was cut, and a hole bored through its centre. One surface of the crystal was coated with a thin layer of white wax. A piece of copper wire was inserted through the hole, and the plate having been placed in a horizontal position, a point on the wire was heated.

The heat travelled along the wire, and part was finally communicated to the crystal. This travelled outwards from the wire, and the square of the distance in any direction to which the wax was melted was taken as proportional to the conductivity in that direction. (Compare with Ingen-Hausz's method, p. 424.) The wax was generally melted over an elliptical or egg-shaped area.

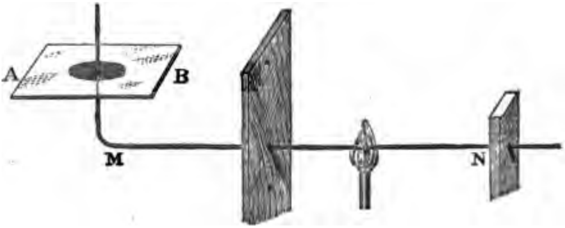

FIG. 200.—De Senarmont's method of determining the thermal conductivities of crystals. (P.)

EXPT. 76.—Substitute a piece of wood about ¼-inch thick, cut parallel to the grain, for the crystal in Fig. 200. Coat the upper surface with paraffin wax, and determine, in the manner described above, the ratio of the thermal conductivities of wood, along and perpendicular to the grain respectively.

More recently Dr. C. H. Lees has attacked the same problem by placing a plate of a crystal between two parts of a metal bar, one end of the compound bar being maintained at a constant high temperature. The conductivity could then be determined by Forbes's method (p. 421).

Conductivity of Liquids.—In order to determine the conductivity of a liquid, special precautions must be taken to avoid the production of convection currents. Hence, in general, the liquid must be heated from above, so that the only method of transmission of heat downwards is by means of molecular exchanges.

EXPT. 77.—Take two long test-tubes and nearly fill these with water. Float a small piece of ice on the surface of the water in one tube, and sink a piece of ice of a similar magnitude to the bottom of the other by the aid of a small lead weight.

Heat the test-tube, in which the ice floats, from the bottom. The ice will quickly melt, owing to the convection of heat from below upwards by the water.

Now hold the other test-tube in a slightly inclined position and heat it at a point just below the surface of the water. It will be found that the water soon boils on the surface, whilst the ice remains almost unaffected at the bottom of the tube.

The above experiment shows that water is a very bad conductor of heat. Most liquids (with the exception of mercury and molten metals generally) are bad conductors of heat.

Determination of the Coefficient of Conductivity of a Liquid—Despretz's Method.—This method is a modification of the bar method of obtaining the coefficient of conductivity of a solid.

A cylindrical wooden vessel B, Fig. 201, about a metre in length and 20 cm. in diameter, was furnished with a number of apertures down one side; through these thermometers were inserted. The vessel was filled with the liquid to be examined. This was first allowed to acquire a uniform temperature throughout, and then hot water was poured into a shallow copper vessel A at the top of the cylinder. The hot water was renewed every five minutes. Observations of the various thermometers showed that a heat wave travelled slowly down the

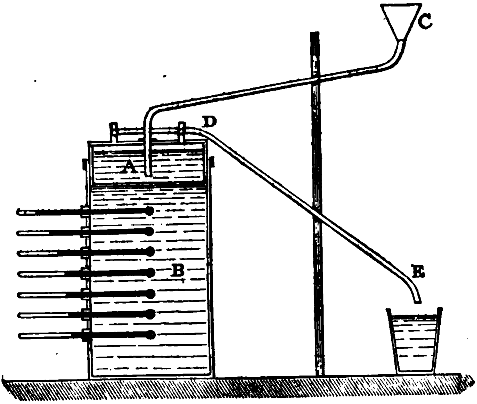

FIG. 201.—Despretz's method of determining the conductivity of water. (P.)

vessel, just as in the case of a metal bar heated at one end. When the thermometers indicated that a constant state had been acquired (which was generally after thirty-six to forty hours), the temperatures indicated by the various thermometers were noted.

Various liquids were treated in this manner, the hot water in A being in each case at the same temperature. The respective conductivities were proportional to the squares of the distances downwards from the copper vessel corresponding to a given fall of temperature. (Compare with the result of Ingen-Hausz's experiment.)

Bottomley's Method.—The above arrangement was modified by Bottomley, two sensitive thermometers placed horizontally one above the other at a small distance apart being employed to determine the fall of temperature per centimetre length near the top of the vessel, whilst the average temperature of the water below that point was indicated by a thermometer with a sufficiently long bulb. From successive readings of the latter thermometer the quantity of heat which passed through the section near the top of the cylinder in one second could be calculated. The vessel A was dispensed with, hot water being poured in a slow stream on to a small wooden float, and withdrawn at an aperture suitably placed after it had spread over the surface of the water B, without, however, mixing with it. The conductivity C was calculated from the formula :—

$$C = \frac{\text{Heat passing through unit area in one second}}{\text{Fall of temperature per cm. at section.}}$$

For water, the value found was C = 0·002.

Numerous other experiments have been performed, for a description of which the student is referred to Preston's *Heat*, Chap. VII. Section II. As a general rule, the results obtained cannot be considered to be so accurate as those obtained in the case of solids.

Conductivity of Gases.—The difficulty of determining the coefficient of conductivity of a gas is enormously greater than in the case of a liquid. In the case of a gas, we have not only convection currents to consider, but errors due to radiation must be provided against. Energy may be propagated through a gas by any or all of the following methods :—

1. *Conduction*, *i.e.*, transfer of energy from molecule to molecule without the production of convection currents. Thermal changes produced in this manner are very small in magnitude.

2. *Convection*, *i.e.*, transfer of heat by the bodily motion of large quantities of heated gas. On the earth such transfers constitute winds, and the rapid variations of temperature often experienced in England when the wind changes, give a sufficiently good idea of the magnitude of the results so produced.

3. *Radiation*, *i.e.*, transfer of energy in the form of waves in the luminiferous ether. In this case the gas molecules, among which the radiation passes, are themselves unaffected, just as the radiation from the sun passes through the atmosphere, without appreciably altering the temperature of the latter. If, however, the radiation falls on the bulb of a thermometer, the latter will be heated, the effect being the same as if the heat had been communicated by the surrounding gas at a high temperature.

As a consequence the most stringent precautions are necessary in experiments on the conductivity of gases. The method which has, up to the present, proved most satisfactory is to determine the rate of cooling of a thermometer bulb, first in a vacuum, and then in the gas in question. In order to eliminate convection currents, the pressure of the gas is reduced. The conductivity is independent of the pressure of the gas, unless this becomes so small that the mean free path of the molecules is comparable with the dimensions of the containing vessel. When the latter stage of exhaustion is reached, a sudden fall in conductivity ensues. It is for this reason that Prof. Dewar's vacuum vessels have proved so valuable in preserving liquefied gases.

The value deduced by Stefan for the conductivity of air, is 0·000056, which is less than one ten-thousandth of the conductivity of copper.

The conductivity of hydrogen is seven times as great as that of air. This is due to the fact that, at a given temperature, a hydrogen molecule is moving more quickly than the average velocity of the molecules composing air. (*See* Chap. XIII.)

Effects of Conduction in Gases.—If a piece of fine platinum wire, through which an electric current is passed, is placed in a glass tube, as in Fig. 202, when the tube is exhausted of air the wire glows brightly. On admitting air the wire becomes dull, owing to the fact that heat is rapidly carried away from it by the air. If the tube is again exhausted, and then filled with hydrogen, the effect is still greater; it is then extremely difficult to make the wire luminous.

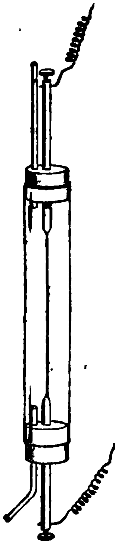

FIG. 202.—Method of showing the effects of the conductivity of a gas. (P.)

Electric glow lamps are exhausted as perfectly as possible, in order that energy should not be carried away from the filament by any inclosed gas. If a small fracture is made in a glow lamp surrounded by an explosive mixture of oxygen and hydrogen, no explosion will occur. The gas conducts the heat away from the filament so quickly that the temperature of the latter falls below the temperature of ignition of the mixture of gases. For this reason glow lamps can be safely used in mines where firedamp is prevalent.

SUMMARY.

Convection of Heat.—When heat is carried from one place to another by the motion of finite parts of a substance, the process is termed convection.

Conduction of Heat.—When heat is propagated from one part of a body to another without the occurrence of motion in any finite part or parts of the body, intermediate points being thereby warmed, the process is termed conduction.

Coefficient of Thermal Conduction of a Substance.—This is defined as the quantity of heat which passes through unit area in one second, divided by the fall of temperature per centimetre length normal to that surface.

Forbes determined the conductivity of metals by heating a bar at one end, and determining the temperature at different points when these acquired constant values, and subsequently observing the rate of cooling of the bar when uniformly heated.

If different bars of similar sectional areas are coated with wax, and have their ends maintained at uniformly high temperatures, the conductivities of the bars are proportional to the squares of the distances through which the wax is ultimately melted.

The Conductivities of Liquids have been determined by heating the surface of the liquids and using a modification of Forbes's method.

Water is a very bad Conductor of Heat.

The Conductivities of Gases have been determined by observing the rate of cooling of a body when surrounded by different gases in a rarefied condition.

QUESTIONS ON CHAPTER XX.

(1) A rod heated at one end has reached a steady state of temperature, and the curve of temperature is known. The rate of loss of heat of the surface for different temperatures is also known. Show how to determine the conductivity of the rod from these data.

(2) Give an account of experiments on the conduction of heat in crystals, and discuss the results obtained.

(3) Describe a method of measuring the thermal conductivity of a bar of iron, and indicate clearly how to calculate the conductivity of the metal from your observations.

(4) Give an experiment which shows that metals are good conductors, and that wood is a bad conductor of heat.

How many gram-degrees of heat will be conducted in an hour through each square centimetre of an iron plate 3 centimetres thick, its two sides being kept at the respective temperatures of 50° C. and 200° C., the mean specific thermal conductivity of iron between these temperatures being 0·12?

(5) Describe a method of determining the thermal conductivity of a metal bar.

(6) Define thermal conductivity. A metal vessel, 1 square metre in area, and whose sides are 0·5 cm. thick, is filled with melting ice, and is kept surrounded by water at 100° C. How much ice will be melted in an hour? The conductivity of the metal is 0·02, and the latent heat of fusion of ice 80.

(7) Describe experiments which have been made to determine the conductivity of iron bars.

A quantity of water is maintained at 100° in a closed iron tank by passing steam into it. If the quantity of steam is 100 grams per second, and if the area of the tank is 6 metres, the thickness of the iron 0·4 cm., and its conductivity 0·2, find the temperature difference between the inside and the outside of the iron.

(8) Some ice is to be kept as long as possible in a warm room. Describe, and give reason for, the construction of a suitable box.

(9) Describe the Davy safety lamp. What thermal principles are applied in its construction?

(10) Define the coefficient of conductivity for heat. What is the coefficient of conductivity of a badly conducting substance upon which the following experiment was made? A tin cylinder, 40 cm. in diameter and 50 cm. in length, is covered all over by a layer of the material 0·33 cm. in thickness. Steam is passed through the cylinder at a temperature of 100° C., and the external temperature being 20° C. water is found to accumulate at the rate of 3 grams per minute. The latent heat of steam at 100° may be taken as 537 gram-calories per gram.

CHAPTER XXI

RADIATION

EVERY one is familiar with the fact, that when the surface of a body is illuminated for some time by a ray of sunlight, the temperature of the body is raised. It may be shown that the sun is the only ultimate source of heat which is of much importance to us on the earth. It has often been pointed out that the heat obtained from burning coal is derived from energy originally stored up under the action of sunlight by the plants from which coal was formed. With the exception of the heat transmitted from the hot interior of the earth, and the small amount of heat which might be obtained by burning the metals which occur in an uncombined state in the earth's crust, we are entirely dependent on the heat which is derived, either directly or indirectly, from the sun.

How then is this heat communicated to the earth at a distance of 90,000,000 miles from the sun? It does not travel from the sun to the earth in the form of *heat* (*i.e.*, energy possessed by vibrating material molecules), since the space intervening between the sun and the earth is free from matter. Nevertheless our knowledge of mechanics renders it necessary for us to consider that energy can only be transmitted from place to place by the motion of *something*. Consequently, we assume that all space is filled with a medium, which possesses no appreciable weight, but which is capable of transmitting energy. This hypothetical medium is termed the *Luminiferous Ether*. By its agency light is transmitted in the form of waves; and we shall see that these waves are capable of setting material molecules in motion, and thus generating heat.

EXPT. 78.—Heat the end of a poker to redness, and throw the shadow of the poker on a white screen by means of an arc lamp (without a lens) or a small acetylene burner. Hot air will be seen to be streaming upwards from the poker, thus constituting convection currents. The air below the poker will be seen to be at rest. Nevertheless, if you place your hand a few inches below the poker, a sensation of heat will be immediately experienced.

In the foregoing experiment, no appreciable amount of heat could have been transmitted to the hand by conduction, since we have already learnt that temperature waves travel through a gas very slowly.

The heat generated in the skin of the hand was due to the absorption of ether waves, similar in many respects to those which, on reaching the eye, produce a sensation of light, and render the hot poker visible in a dark room.

"Radiant Heat."—When the poker, in the above experiment, has so far cooled that it is no longer luminous, a sensation of heat is still experienced if the hand is placed at some distance beneath it. Hence some ether waves, the absorption of which produces heat, are not capable of producing the sensation of light.

The term "*radiant heat*" has been applied to those non-luminous ether waves which, when absorbed by a body, raise the temperature of the latter. It must be remembered, however, that whilst passing through space, these waves are not associated with the motions of material molecules, and do not, therefore, strictly speaking, constitute *heat*. "Thermal radiation" would be a better title for this method of transmission of energy.

Methods of Detecting Thermal Radiations.—If sunlight, or the radiation from a piece of heated metal, is allowed to fall on the bulb of an ordinary mercury thermometer, a rise of temperature will be indicated. If the bulb is coated with a layer of dead black paint,[1] the rise of temperature will be much increased.

A form of *Leslie's differential air thermometer*, which may be easily and cheaply constructed, is shown in Fig. 203. Two round-bottomed flasks are provided with sound corks, each pierced to admit two glass tubes, bent as shown in the figure. The shorter glass tube is, in each case, fitted with a piece of india-rubber tubing, which can be closed by a piece of glass rod. The longer glass tubes are connected, by means of pieces of india-rubber tubing, to the ends of a glass manometer tube containing some coloured water. If the flasks are supported in the manner indicated in Fig. 203, they can be used hanging down, as shown, or they may be rotated into an erect position, similar to that indicated in Fig. 211. The flasks should be coated on their external surfaces with dead black paint.

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[1] Dead black paint may be made by mixing lamp black with alcohol, in which a small amount of shellac has been dissolved. Sufficient shellac should be used to render the paint adhesive to glass, but not enough to produce a glossy black surface.

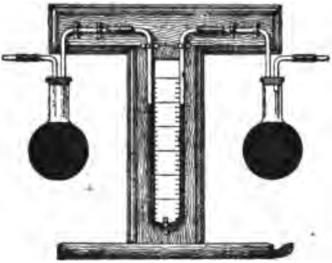

FIG. 203.—Leslie's differential air thermometer.

Fig. 204 represents a comparatively sensitive arrangement for detecting thermal radiations. It consists of two bulbs, connected by means of a glass tube, the internal space, which contains a quantity of coloured ether, being exhausted of air. The liquid ether acts as a pressure indicator, whilst its vapour fills the two bulbs. The lower bulb is blackened, and when radiations are absorbed by it, a large expansion of the ether vapour is produced.

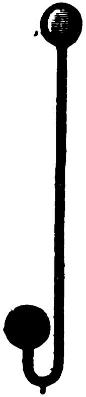

FIG. 204.—Ether thermoscope.

Thermal radiations may also be detected and measured by allowing them to fall on one face of a thermopile, the other face being maintained at a constant temperature by being covered with a brass cap. The necessary electrical arrangements have been indicated in Chap. XIX.

Langley's bolometer and Boys's radio-micrometer afford still more delicate means of detecting thermal radiations.

Properties of Thermal Radiations.

(1) *Thermal radiations can be transmitted through a vacuum.*——This was proved by Sir Humphry Davy, who placed a black bulb thermometer at some distanc

from a spiral of platinum wire which could be heated to redness by an electric current, and enclosed both in a vessel which was afterwards freed from air. When the platinum wire was heated, the black bulb thermometer indicated a similar rise of temperature to that which occurred when the vessel was full of air.

(2) *Thermal radiations are transmitted in straight lines, like beams of light.*

EXPT. 79.—Coat one side of a sheet of tinfoil with paraffin wax, and the other with dead black paint. Cut a star-shaped aperture from another sheet of tinfoil, and hang the two sheets vertically and parallel to each other at a distance of 2 or 3 inches apart, the blackened surface of the first sheet being on the inside. Heat an iron ball to a white heat, and support this so that part of the radiations emitted can pass through the star-shaped aperture and fall on the blackened surface of the first sheet.

After a few minutes the paraffin wax will be seen to be melted over a star-shaped area, corresponding to the aperture cut in the second sheet of tinfoil. The sharpness of the edges will depend on the size of the iron ball used, and the distance from the aperture at which it is placed; just as the sharpness of the shadow of an object depends on the size and position of the source of light.

(3) *Thermal radiations are reflected from polished metallic surfaces, and obey the same laws as light.*

EXPT. 80.—Two tin-plate tubes, of about 3 inches diameter and 30 inches long, together with a sheet of polished tin-plate supported in a vertical plane on a suitable stand (*see* R, Fig. 205), are required for this experiment, in addition to the iron ball B and the ether thermoscope T. Support the tubes in a horizontal plane, so that they are inclined to each other at about 120°, as shown in Fig. 205. Place the heated ball and the thermoscope in position, the sheet of tin-plate R being removed. No appreciable effect will be produced on the thermoscope. Now place the sheet of tin-plate R in position, and rotate it till the thermoscope shows the greatest effect. This will occur when the two tubes are equally inclined on opposite sides of the normal to R.

EXPT. 81.—Obtain two concave metal mirrors, and support these facing each other at about a metre apart. Place the iron ball, heated to redness, at the principal focus of one mirror, and the black bulb of the ether thermoscope at the principal focus of the other.

It will be found that the ether thermoscope indicates a considerable rise of temperature when it is placed at the focus, but that when it is moved away from that point through a short distance, the temperature falls to its normal value.

(4) *Thermal Radiations can be Refracted.*—If a continuous spectrum is formed in the usual way, using a prism to analyse sun-light, and various parts of the spectrum are successively thrown on the blackened face of a thermopile, or, better still, on the small blackened copper disc of Boys's radio-micrometer (p. 410), various thermal effects will be indicated. Starting at the violet end of the spectrum, a very small heating effect will be observed. Proceeding toward the red end of the spectrum, the heating effect becomes greater and greater. When the limits of the visible spectrum are reached, a considerable heating effect is indicated, and in proceeding beyond this limit the effect becomes greater still.

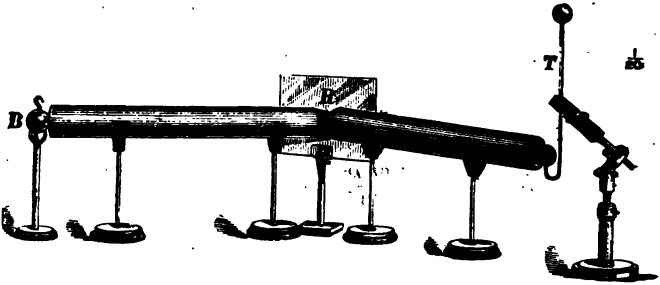

FIG. 205.—Arrangement for examining the law of reflection of thermal radiation.

In performing an experiment such as the above, it must be remembered that a substance which is transparent to one part of the spectrum, may be partially or totally opaque to another part of it. Thus, a solution of magenta (or fuchsine) in alcohol is transparent to red light, but is opaque to the green and blue part of the spectrum. Similarly glass, which is transparent to those rays which are capable of exciting a sensation of light, is opaque to that part of the spectrum which extends beyond the red limit of the visible spectrum, and which produces the greatest heating effect. Hence, when experiments are to be performed with regard to the infra-red spectrum, a prism of rock-salt, or sylvine (a crystalline variety of potassium chloride, possessing properties similar to those of rock salt), is used. These substances are transparent to the greater part of the infra-red spectrum.

It has been found that if the radiation from a vessel filled with boiling water is analysed by means of a prism of one of the above substances, and examined by the aid of a radio-micrometer or a bolometer (pp. 410 and 404), such radiations are found to be deviated to a smaller extent than red light would be. It is proved, in works on Light, that blue light, which consists of radiations of short wave-length, is deviated by a prism to a greater extent than red light, which comprises radiations of longer wave-length.

Hence, since non-luminous thermal radiations are deviated still less than red light, we conclude that such radiations consist of very long waves.

It must not be concluded that hot bodies alone emit thermal radiations. Langley has been able to measure the radiation emitted by ice, and by a still colder body, the moon. Indeed, the only condition in which a body would be incapable of emitting radiations, would correspond to its existence at the absolute zero of temperature. In this condition its constituent molecules would be absolutely quiescent, and consequently incapable of disturbing the luminiferous ether, and thus emitting radiations.

If a white-hot body is gradually cooled, after a time the light emitted becomes red, and then vanishes. Thermal radiations are, however, still emitted. Conversely, as a body is heated, radiations of shorter wave-lengths are emitted.

In order that a body should emit pure white light, it must be heated to about the temperature of melted platinum. This is about the temperature to which the carbon filaments in electric glow-lamps are raised.

(5) *Thermal radiations can be polarised.*—It is also proved in works on Light, that the vibrations which constitute a light wave are performed in a plane at right angles to the direction of propagation, *i.e.*, at right angles to the ray of light. In a ray of light emitted from a candle, vibrations take place in all directions at right angles to the ray. This is indicated in Fig. 206 by the double arrows at right angles to each other.

When a ray of light is reflected from a mirror, the plane containing the ray and the normal to the mirror at the point of incidence is called the plane of incidence.

Now it is found that if a ray of light is reflected, at a certain angle, from a sheet of blackened glass, only those vibrations which are perpendicular to the plane of incidence are reflected.

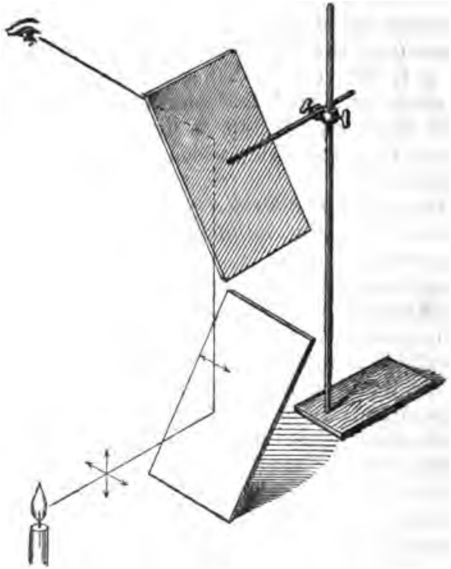

FIG. 206.—Isometric projection of arrangement for showing the polarisation and extinction of light by reflection.

This is indicated in Fig. 206 by the double arrow representing the single direction of vibration in the reflected ray. It is easily seen that these vibrations are parallel to the surface of the mirror. Those vibrations which, as it were, *cut into* the glass, are absorbed. The ray of light, which now only possesses vibrations parallel to a certain direction, is said to be *polarised by reflection.*

If this ray falls on a second mirror of black glass, at an equal angle of incidence, those vibrations which are in the plane of incidence will not be reflected. If the second mirror is arranged, as in Fig. 206, so that the vibrations of the polarised ray are in the plane of incidence, and therefore cut into the glass, an eye placed as shown will be unable to see an image of the candle flame. The light has been polarised by reflection from the first mirror, and extinguished by reflection from the second mirror.

If, now, a hot body is substituted for the candle flame, and a radio-micrometer for the eye in Fig. 206, it is found that the thermal radiations are extinguished in a similar manner. If the inclinations of the mirrors to the horizon are altered by a few degrees, it is found that thermal radiations now reach the radio-micrometer. In similar circumstances the image of the candle flame could be perceived by the eye. Hence, thermal radiations can be polarised like light waves.

(6) *Thermal radiations are propagated in space with a velocity equal to that of light.*—This has been proved by observing that when a total eclipse of the sun occurs, thermal radiations cease to reach the earth at the instant when the light is extinguished.

Finally, we see that we must consider non-luminous thermal radiations (or radiant heat) to consist of vibrations of the ether similar in every respect to light waves, except that the length of a wave is greater. Consequently, with an eye suitably constituted, we should be able, for instance, to see a person in a perfectly dark room, by virtue of the radiations emitted from his body.

It is possible that animals which seek for their food in the night-time actually possess this capacity for perceiving objects by virtue of the thermal radiations emitted.

(7) *The heat produced per second, at a surface of given area, by the absorption of thermal radiations emitted by a body at a constant temperature, is inversely proportional to the square of the distance between the body and the absorbing surface.*

This can be proved by placing an electric glow-lamp at various distances from one face of a thermopile, and observing the galvanometer deflections produced. These deflections will be nearly proportional to the rate of absorption of thermal radiations, or to the heat thus produced. The face of the thermopile used to absorb the radiations should be shielded from air currents by means of a conical reflector (Fig. 184); the other face should be covered by a brass cap. If the outer surface of the glow-lamp is coated with dead black paint, a better result will be obtained.

The law above enunciated will be found not to hold when the distance between the lamp and the thermopile is made so small as to be comparable with the linear dimensions of the lamp.

Constitution of the Spectrum.—In some of the older text-books, it may be found stated that the spectrum consists of non-luminous actinic rays of short wave-length, of luminous rays of longer wave-length, and of thermal or dark heat waves of still greater wave-length. This classification is, however, essentially arbitrary. All rays of the spectrum are capable of producing chemical changes in certain substances. The ultra-violet waves were termed actinic on account of the accidental circumstance that these waves are very active in causing the blackening of silver chloride and silver bromide. On the other hand, it is yellowish-green light which is active in promoting the decomposition of carbon dioxide, effected by the chlorophyll in the leaves of plants; and Captain Abney has been able to prepare photographic plates which are sensitive to non-luminous thermal radiations, so that a kettle of boiling water might be photographed in a dark room.

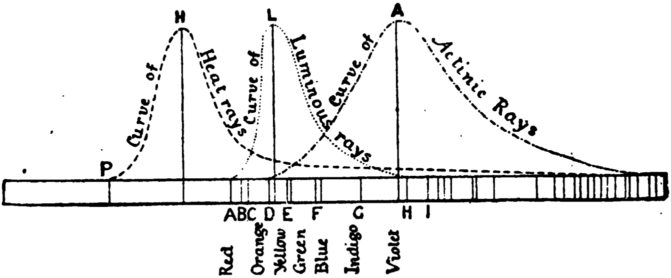

FIG. 207.—Thermal, luminous, and chemical properties of different parts of the solar spectrum.

Further, the absorption of light of any wave-length is capable of raising the temperature of the absorbing body.

Fig. 207 shows the luminosity, the heating capacity, and the chemical activity (in regard to silver salts) of various parts of the solar spectrum. The form of the luminosity curve depends on the nature of our eyes, and the chemical activity will vary with the nature of the chemical compound acted upon. The "curve of heat rays," however, represents a definite physical property of sunlight. It represents the energy of the ether vibrations of various wave-lengths.

Fig. 208 is taken from a paper by Dr. Snow,[1] and represents the energy radiated from the heated vapours constituting the electric arc (*not* the energy radiated from the heated carbons). The small scale, from H to A, at the bottom left-hand side of this diagram, represents the extent of the visible spectrum. Wave-lengths are plotted as abscissae, and energies as ordinates. The curve was obtained by the use of a spectrometer and a very sensitive modification of Langley's bolometer. It at once

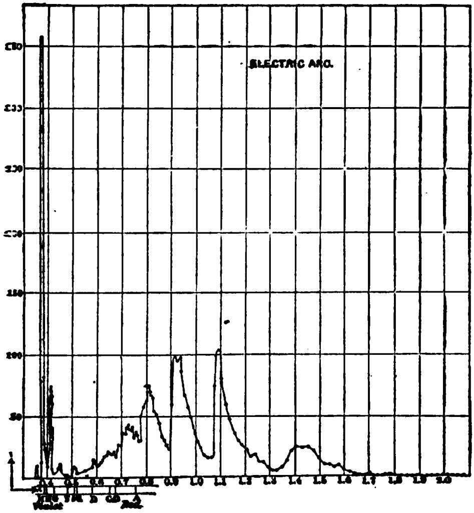

FIG. 208.—Energy radiated from the heated gases constituting the electric arc.

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[1] "On the Infra-red Spectra of the Alkalies," by B. W. Snow. *Physical Review*, vol. i. p. 28. 1893.

becomes apparent that the greatest amount of energy was radiated in connection with short waves near the violet limit of the visible spectrum. It is these violet waves which give the light from an electric arc its characteristic colour.

Diathermancy.—When white light passes through a material substance, some of the waves, of particular wave-lengths, may be absorbed, the transmitted light consequently becoming coloured. In a similar manner, when non-luminous thermal radiations pass through a material substance, certain wave-lengths are absorbed, and others are transmitted. A substance which transmits radiations of a certain wave-length is said to be *diathermanous* for those radiations. A substance which absorbs radiations of a particular wave-length is said to be *athermanous* for those radiations.

An interesting example of the selective absorption (absorption of radiations of a particular wave-length) is furnished in the case of glass. A ray of sunlight is only slightly affected by passing through a sheet of glass, and the glass is scarcely heated. On the other hand, the use of glass for fire-screens shows that the radiations emitted by glowing coal are plentifully absorbed by glass. Further, a sheet of glass, after being held in front of a fire for a few minutes, becomes unpleasantly hot to the touch.

Some substances (*e.g.*, lamp black) are generally athermanous, that is, they absorb radiations of all wave-lengths.

Much interesting work has been performed in relation to the diathermancy of various substances. Until recently, however, investigators, almost without exception, omitted to determine the wave-length of the radiations with which they experimented. As a consequence, much confusion and many contradictory conclusions may be found amongst the results obtained by the earlier experimenters. This is hardly to be wondered at; a similar confusion as to optical transparency would result if the wave-length or colour of the light used were not specified. In that event, an experimenter, who worked with red light, might have maintained that a solution of magenta was transparent, whilst another, who used green light, might have maintained, with equal justness, that such a solution was opaque.

It will be proved later that the nature of the radiations emitted by a body depends on the character of the surface, and also on its temperature. Consequently much of the earlier work respecting diathermancy must be taken as referring to radiations emitted by a certain surface, maintained at a specified temperature.

Melloni's Experiments.—Fig. 209 represents the apparatus used by Melloni, set up, however, to determine the laws of reflection of thermal radiations. A is a lamp with a reflector, C is a screen with a circular aperture, D is a table carrying a mirror, silvered and polished on its front surface, and E is a thermopile. The double screen B is removed during the course of an experiment. Another screen intercepts direct radiations from the lamp to the thermopile.

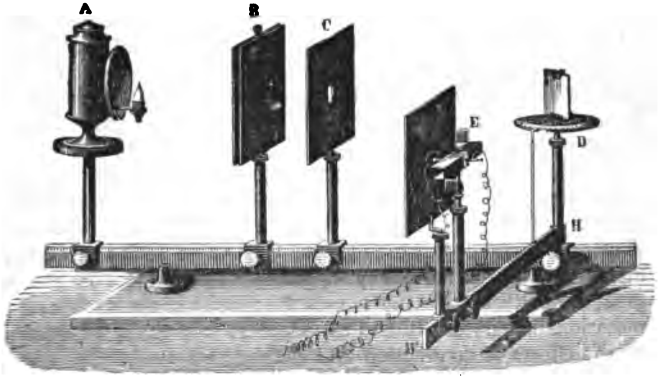

FIG. 209.—Melloni's apparatus.

When investigating diathermancy, the mirror D was replaced by the thermopile E. The double screen B being removed, radiations passed from the lamp or other source through the aperture in C, and finally fell on the blackened face of the thermopile. This latter was connected with a sensitive astatic galvanometer, and the consequent deflection of the latter was observed. Plates of various substances were then successively placed over the aperture in C, and the deflections observed. The amount by which the galvanometer deflections were diminished by covering the orifice in C with different plates gave a means of estimating the relative athermancies of the substances.

Rock-salt was found to be particularly transparent to thermal radiations, whilst a plate of crystalline alum was particularly opaque. Ice was found to be still more opaque. Distilled water was found to be exceedingly athermanous, whilst an aqueous solution of alum or sugar was slightly more diathermanous. This latter result, which has since been verified, disproved at very common belief (which has not quite disappeared at the present day), that an alum solution is very opaque to thermal radiations.

Melloni considered rock-salt to be transparent to radiations of all wave-lengths. Balfour-Stewart, however, showed that a plate of rock-salt is extremely opaque to the radiations emitted by a piece of heated rock-salt. This is an instance of the law, to be discussed later, that a substance is opaque to radiations which it emits when heated.

Diathermancy of Gases. Tyndall's Experiments.—Previous to 1859, it was generally considered that gases were perfectly transparent to thermal radiations. In that year Professor Tyndall commenced an exhaustive series of experiments on the diathermancy of gases. The subject is one of great difficulty, since in most cases the opacity of a gas to thermal radiations is very small, and experiments may easily be vitiated by the effects of conduction and convection.

To overcome these and other difficulties, the arrangement represented in Fig. 210 was used. The source of heat was a cube C of cast copper filled with water, which was kept boiling by the aid of a lamp. The radiating face formed one side of a metal vessel V, which was continuous with a short metal tube F. The end of this tube was separated by means of a plate of rock-salt from the experimental tube SS′. The vessel V could be exhausted, so that the radiations traversed a vacuum before entering the experimental tube. Conduction of heat from the metal cube C to the end of the experimental tube was prevented by the circulation of a stream of cold water round the vessel V.

The end S′ of the experimental tube was also closed by a plate of rock-salt. After passing through the experimental tube, the radiations fell on one face of a thermopile P. The deflection of the galvanometer with which P was connected, was dependent on the difference in temperature between the two opposite faces of the thermopile. Hence, by placing a second cube full of boiling water C′ opposite the back surface of the thermopile, and partially screening the latter by means of the plates E, the needle of the galvanometer could be brought to its zero position.

An experiment was performed in the following manner. The experimental tube SS′ was thoroughly exhausted, and the cubes C and C′ having attained their final temperatures, the screens E were adjusted to cut off part of the radiation falling on the back surface of P, until the galvanometer needle was brought to its zero position. Pure dried gas was then introduced into the experimental tube. Any deflection of the galvanometer thus produced must have been due to the absorption in the experimental tube of the radiations emitted by C.

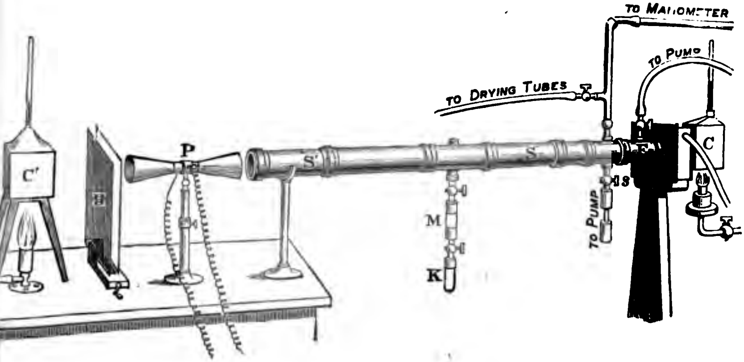

FIG. 210.—Tyndall's arrangement for investigating the diathermancy of gases. (P.)

It was found that the introduction of oxygen, hydrogen, nitrogen, or air produced an almost inappreciable effect. When, however, the tube was filled with olefiant gas, more than 70 per cent. of the total radiation was found to be absorbed. Carbon dioxide and ammonia were also found to absorb thermal radiations very strongly.

The following table gives the percentage of the total radiation emitted by the cube C, which was absorbed by a column, four feet long, of various gases at atmospheric pressure.

Substance	Percentage of Energy absorbed.	Substance.	Percentage of Energy absorbed.
Air	·08	Carbon dioxide	7·1
Oxygen	·08	Nitrous oxide	28
Nitrogen	·08	Sulphuretted hydrogen	31
Hydrogen	·08	Marsh gas	32
Chlorine	3·1	Sulphurous acid	56
Hydrochloric acid gas	4·9	Olefiant gas	71
Carbonic oxide	7·1	Ammonia	94·5

The diathermancy of various vapours was also examined. A tube K, Fig. 210, provided with a stop-cock, was partly filled with the liquid the vapour of which was to be examined, and the space above the liquid was then exhaused of air. The stop-cock having been closed, the tube K was screwed in position, and the experimental tube was exhausted. The needle of the galvanometer having been brought to rest by the adjustment of the screen E, the stop-cock with which the tube K was provided was opened, and the vapour of the liquid thus allowed to fill the experimental tube. Absorption of the radiations was indicated, as in the cases where gases were used, by a deflection of the galvanometer needle.

It was found that the percentage of the total radiation which was absorbed was dependent on the temperature of the source. Thus, some substances absorbed a great part of the radiation emitted by a platinum spiral heated by an electric current so as to be just faintly luminous, whilst a much smaller proportion of the total radiation emitted by the spiral at higher temperatures was absorbed.

Tyndall also found that certain perfumes exhibited marked absorptive properties. In some cases the merest trace of a perfume produced appreciable effects. This is not altogether without parallel, for ·000001 gram of magenta dissolved in a cubic centimetre of water acidulated with a little acetic acid produces a marked colouring. Tyndall's results, however, need verification.

Aqueous Vapour.—Tyndall found that when the experimental tube was filled with air saturated with aqueous vapour, the absorption was 72 times as great as if the tube had been filled with dry air. In other words, a column of air saturated with aqueous vapour, possessing a length of about four feet, absorbs about 5 per cent. of the radiation emitted by a heated metal surface.

The same subject has also been experimentally investigated by Magnus and others. Magnus found that dry air was slightly opaque to thermal radiations, whilst the absorption was unaffected by the presence of aqueous vapour. On the whole, however, Tyndall's experiments have the appearance of being most trustworthy.

More recently Rubens and Paschen have found that when thermal radiations, which have been passed through a vessel containing saturated aqueous vapour, are analysed by a prism of sylvine, and the resulting spectrum is examined by the aid of a sensitive bolometer, certain well defined absorption bands can be detected, thus showing that aqueous vapour is opaque to radiations of certain wave-lengths, but, comparatively speaking, transparent to those radiations forming the greater part of the spectrum.

Discrepancies between the results obtained by different experimenters may therefore have originated in the employment of radiations of different wave-lengths.

Radiation of "Cold."

EXPT. 82.—Place a block of ice at a short distance from one of the blackened bulbs of the differential air thermometer described on p. 438, the other bulb being surrounded by a tin can. It will be found that the motion of the column of coloured water indicates that the exposed bulb has been cooled, as though "cold" were radiated from the ice.

The true explanation of the above experiment is as follows: When the exposed bulb of the thermometer was surrounded by bodies at a temperature equal to its own, radiations were emitted by the bulb to the surrounding bodies, whilst radiations emitted from those bodies were absorbed by the bulb, so that its temperature remained constant. The block of ice served to screen the black bulb from the radiations emitted by surrounding bodies, so that more energy was radiated from the bulb than was received by it. Consequently the bulb was cooled.

Theory of Exchanges.—The above explanation of the cooling of a body when placed in the neighbourhood of a cold body, was given in 1792 by Prévost of Geneva. It is seen to depend on the assumption that when a number of bodies are placed in the neighbourhood of each other, each body emits radiations in all directions, and at the same time absorbs radiations emitted by the surrounding bodies. Thus a system of exchange is in action.

The foundation for this theory will be understood from the following reasoning. If a number of bodies, initially at different temperatures, are placed in a vessel, the walls of which are impervious to heat, then if no heat is generated in the inclosure, the bodies will finally attain a uniform temperature. This will happen whether the bodies are surrounded by air and placed in contact so that convection and conduction of heat may occur, or whether they are hung by fine silk fibres, and the space separating them is exhausted of air, so that energy can only enter or leave a body in the form of radiations.

Now, at a constant temperature, the energy possessed by the vibrating molecules of a body must possess a constant value. But the moving molecules of a body disturb the ether, and so generate waves which carry energy away from it. Therefore if no energy were communicated to the body its temperature would continually fall. Consequently, since the temperature of the body remains constant, energy must be absorbed at a rate equal to that at which it is radiated. Finally, since energy is supposed to be unable to pass through the walls of the inclosure, the energy absorbed by a body must have been radiated by the other bodies contained in the inclosure.

Application of Prevost's Theory.—(1) Let us suppose that two masses of silver, one possessing a polished surface, whilst the surface of the other has been covered with lamp black, are placed in the same inclosure. A polished silver surface is known to reflect the greater proportion of the radiation which falls on it. Consequently the body with the polished silver surface can absorb only a small amount of the energy radiated by the other body. Therefore, in order that its temperature should not fall, it must radiate only a small amount of energy. In other words, a surface which has an inferior absorbing capacity will also possess an inferior capacity for emitting radiations.

On the other hand, the blackened surface which absorbs nearly all the radiations which fall on it, must also emit radiations freely, or the temperature of the body would continually rise.

Therefore, a surface which absorbs radiations freely must also be able to emit radiations freely.

Expt. 83.—Take a sheet of tinfoil, and cover one surface with a coat of mercuric iodide ground up with water containing a little gum. (Mercuric iodide is a scarlet powder at ordinary temperatures, but becomes yellow when heated to 150° C.) Paint any design with dead black paint on the other surface of the tinfoil. Heat a flat piece of iron to a red heat, and hold it, at a distance of about two inches, in front of the design on the polished surface of the tinfoil. After a short time, the design will be seen to be reproduced in yellow on a scarlet ground on the other side of the tinfoil. This proves that a black surface absorbs thermal radiations more readily than a polished surface.

Expt. 84.—Obtain a biscuit tin, fit the lid on it, and bore a hole in the latter for the introduction of water. Coat one face with dead black paint, and leave the opposite one polished. The two remaining faces may be respectively coated with paper and shellac varnish. You have thus made a *Leslie's cube.*

Turn up the bulbs of the differential air thermometer so as to assume the positions shown in Fig. 211. Place the Leslie's cube between the two bulbs, with the blackened surface towards one bulb and the bright surface towards the other. Pour boiling water into the cube. Both surfaces of the latter will now be at the same temperature, but the motion of the liquid in the manometer at once indicates that more heat is generated by the absorption of the radiations emitted by the black surface of the cube than from those emitted by the bright surface.

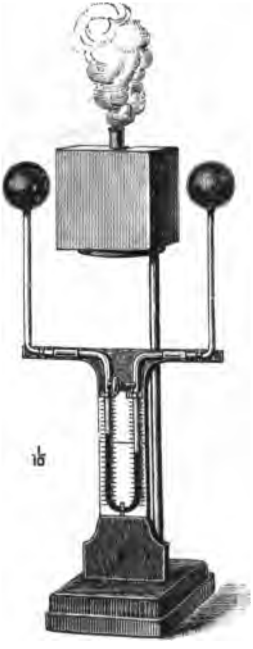

Fig. 211.—Arrangement for showing that a black surface emits radiations more readily than a polished one.

Since the black surfaces of the thermometer bulbs absorb all radiations which fall on them, it follows that the black surface of the cube emits radiations more readily than the opposite polished surface.

EXPT. 85.—Obtain a piece of a white china plate possessing a dark design (A, Fig. 212). The dark parts of this design absorb light, whilst the white parts simply scatter the light falling on them.

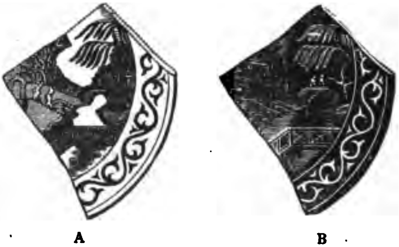

FIG. 212.—Piece of "willow pattern" china—(A) when cold; (B) when raised to a high temperature.

Now heat the piece of plate in a furnace. On removing it, it will be seen that the pattern is reversed (B, Fig. 212), the black parts now appearing bright, and the white parts dark.

This experiment shows that *the same kind of radiation is emitted from a surface as is absorbed by that surface.*

(2) Let us suppose that two pieces of rock-salt, at different temperatures, are placed in an inclosure, which is freed from air and provided with non-conducting walls. Then, since both pieces of rock-salt ultimately attain a common temperature, energy must be radiated from the hot to the cold piece. But rock-salt is transparent to most non-luminous thermal radiations, *i.e.*, such radiations will pass through it without being absorbed, and therefore without raising its temperature. But since the hot piece of rock-salt cools, thermal radiations of a certain wave-length must be emitted from it. And, since the cold piece of rock-salt is at the same time heated, the radiations emitted by the hot piece of rock-salt must be absorbed by the cold piece.

Hence, we see that theory indicates that the same kind of radiation which is emitted from a surface can also be absorbed by that surface.

Emissivity of a Surface.—The quantity of energy given up by unit area of a surface in one second, per unit difference of temperature between the surface and surrounding bodies, is termed the *emissivity of the surface.*

The first trustworthy experimental determination of the emissivity of a surface was made by Dr. D. M'Farlane, under the direction of Lord Kelvin, in 1871. A copper sphere with a blackened surface was hung inside a double-walled tin-plate vessel, the inside being coated with lamp black, and the space between the walls filled with water. The temperature of the sphere from moment to moment was observed by the aid of a thermo-couple, one junction of which was inclosed in the sphere.

Dr. Bottomley has more recently determined the emissivity of a long platinum wire stretched inside a copper cylinder which was blackened on its inside surface. The wire was heated by means of an electric current, and when a steady state was attained, the electrical energy dissipated in any time in the wire must be emitted by the surface of the wire in the form of radiations, or carried away by conduction and convection.

Quite recently Mr. J. E. Petavel[1] has attacked the same problem in a similar manner. A piece of platinum wire of about one square millimetre sectional area was heated by an electric current. The energy dissipated by the surface of a given length of the wire was obtained by multiplying the difference of potential between the extremities of this length of wire, by the current which flowed through it. Both the last mentioned quantities were directly observed. From the same data the electrical resistance of the wire was calculated, and the temperature of the wire was then determined in the manner described in connection with the platinum pyrometer (p. 400).

The emissivity of the platinum surface, in therms per sq. cm. per second per degree centigrade difference of temperature, between the wire and the walls of its enclosure, when the wire was surrounded by gases at various pressures, is exhibited in

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[1] "On the Heat Dissipated by a Platinum Surface at High Temperatures." J. E. Petavel. *Phil. Trans.*, vol. 191, pp. 501–524. 1898.

Fig. 213. The high emissivity when the wire was surrounded by hydrogen is specially noticeable. It may further be remarked that the presence of moisture in the air increased the emissivity.

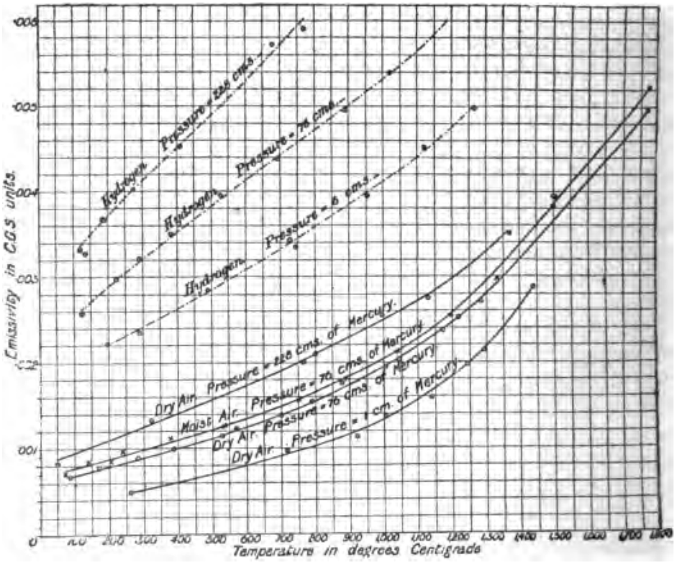

FIG. 213.—Emissivity of a platinum surface, in different gases. (Petavel.)

Laws of Cooling.—Many attempts have, from time to time, been made to determine experimentally the relation between the rate of cooling of a body in a vacuum and the temperature of the body.

Newton's Law of Cooling, viz., that the heat radiated per second is proportional to the difference of temperature between the body and its surroundings, has already been mentioned (p. 129). The law represents the results of experiments at low temperatures, but fails when the temperature of the radiating body is high.

Dulong and *Petit* executed a number of experiments relative to the rate of cooling of mercury in glass thermometers when placed in a vacuum. These experiments were naturally subject to the errors incidental to the use of mercury thermometers for the measurement of temperatures. Further, no great range of temperature could be obtained. As a result, they proposed the formula

$$R = E_1 . 1{\cdot}0077^T$$

where R is the rate at which energy is radiated from the body at an absolute temperature T, and E_1 is a constant. This formula does not agree with the results of experiments at high temperatures.

From the results of Dulong and Petit's experiments, *Stefan* proposed the formula

$$R = E_4T^4$$

where R and T have the same signification as above, and E_4 is a constant. This law has been verified on theoretical grounds, but is not in agreement with the experimental results obtained by some investigators.

Stefan's "fourth power law" does not mean that the rate of cooling of a body is proportional to the fourth power of the temperature, but that the amount of energy radiated per second is proportional to that quantity. If a body at an absolute temperature T_1 is placed in an inclosure exhausted of air, and the walls of the inclosure are maintained at an absolute temperature T_2, then, since the walls are radiating energy to the body at a rate proportional to T_2^4, we have

$$\text{Rate of cooling of body} = C(T_1^4 - T_2^4)$$

where C is a constant.

Weber has proposed the law expressed by

$$R = E_2 . T . 1{\cdot}00043^T$$

where E_2 is a constant.

The most satisfactory methods of experimentally determining the law of radiation of energy are :—

(1) To determine the amount of electrical energy dissipated in a platinum wire, maintained at a high temperature by means of an electric current, after the manner described above in connection with Petavel's experiments, except that the wire is placed in an inclosure freed from air as perfectly as possible. It is impossible, however, to obtain a perfect vacuum, and any residual gas will tend to *conduct* heat away from the wire. For very high temperatures, the platinum will itself be vaporised. Hence, when this method is used, the results obtained will give too great a rate of radiation for a given temperature.

(2) The radiations, emitted from a wire maintained at a known temperature by means of an electric current, may be received on

a bolometer or other sensitive radiometer. In this case, all the radiations may not be absorbed by the blackened surface or the radiometer, so that too small a rate of cooling will result.

Temperature of the Surface of the Sun.—One of the chief sources of interest in connection with laws of cooling is that they afford us, in conjunction with other experimental

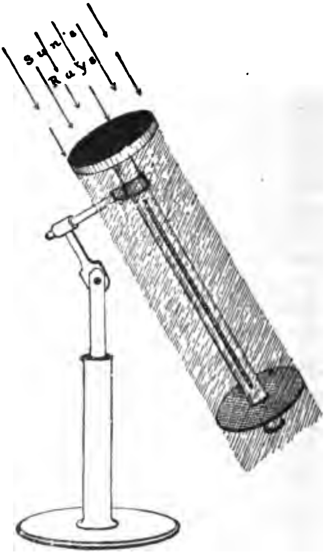

Fig. 214.—Pyroheliometer.

data, a means of estimating the temperature of the sun's surface.

If we knew the rate at which thermal radiations are emitted from unit area of a body for all temperatures, and could experimentally determine the amount of energy emitted per second, from the surface of a body of known size, then it is plain that we could obtain the temperature of the surface of that body.

The amount of energy radiated from the sun per second has been determined by Pouillet, using an instrument called the *Pyroheliometer.* This instrument is represented in Fig. 214. It consists of a flat cylindrical vessel of platinum, attached to and in internal communication with a metallic tube, which ends in a circular disc. The diameter of this disc is equal to that of the cylindrical vessel. The vessel and tube are filled with mercury, the temperature of which is indicated by a thermometer in the tube. The top surface of the cylindrical vessel is coated with lamp black.

In making an observation, the initial temperature of the mercury, as indicated by the thermometer, is observed, and the black surface of the cylindrical vessel is then turned toward the sun, and adjusted so that the shadow of the vessel just covers the disc at the end of the tube. In this position the solar radiations fall vertically on the black surface, and are absorbed. After a certain interval of time the black disc is covered with a cap, and the mercury is shaken up so as to ensure that the whole is at a uniform temperature. This temperature is observed by the aid of the thermometer. A correction for loss of heat by radiation may be applied, using the method explained on p. 131. The mass and specific heat of the inclosed mercury being known, the amount of heat generated by the absorption of the solar radiations falling on a surface of known area in a known interval of time can be calculated.

From this, the total amount of energy which passes, in one second, through the entire surface of an imaginary sphere of which the sun is the centre, and the distance from the sun to the earth is a radius, can readily be calculated. This latter will be equal to the energy leaving the sun's surface in a second, and thus the energy emitted from each sq. cm. of the sun's surface per second can be calculated, the diameter of the sun being known.

Now, from the law of cooling adopted, the temperature corresponding to the above rate of emission of energy per unit area of a body can be determined. For instance, assuming Stefan's fourth power law to be correct, and that the rate of radiation from the surface of a platinum wire at some high temperature is known, we can calculate the temperature at which the rate of radiation would be equal to that found for the sun's surface. The value so obtained will be equal to the temperature of the sun's surface.

Using Newton's law of cooling, a temperature of 1,000,000° C.

is thus found for the sun's surface. This value is unquestionably too high.

The following table, taken from an account of a lecture[1] delivered at the Royal Institution by Professor Callendar, gives the temperature of the sun's surface as deduced with the aid of the various laws of cooling mentioned. The value deduced from Rosetti's experiments is probably much too high, whilst that deduced from Dulong and Petit's cooling formula errs in the opposite direction.

THE TEMPERATURE OF THE SUN'S SURFACE DEDUCED FROM VARIOUS LAWS OF COOLING.

Observers and date.	Temperature measured by	Radiation observed by	Formula proposed.	Solar temp. deduced.
				°C.
Dulong and Petit (1817)	Mercury thermometer	Rate of cooling in vac.	$E_1\ 1\cdot0077^T$	1,900
Rosetti (1878)	Mercury thermometer	Thermo-pile Sb–Bi	E_3T^3 (nearly)	12,700
Stefan (1878)	No experiments made.		E_4T^4	6,900
Schleiermacher (1885)	Platinum resistance	Heat loss C^2R in vac.	E_4T^4	6,900
Weber (1888)	No experiments made.		$E_2T\ 1\cdot00043^T$	2,450
Bottomley (1888)	Platinum resistance	Heat loss C^2R in vac.	$E_6T^{5\cdot7}$*	4,000
Paschen (1893)	Thermo-couple Pt–Pt Rh	Bolometer.	$E_6T^{5\cdot7}$*	4,000
Wilson and Gray (1897)	Platinum expansion	Radio-micro-meter	E_4T^4	6,900
Petavel (1898)	Platinum resistance	Bolometer.	E_5T^5*	4,800

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[1] See *Nature*, vol. 59, March, 23, 1899, p. 495.

* Formulæ deduced by Professor Callendar from observations of the authors mentioned.

SUMMARY.

Radiation. The molecules of a heated body being in motion, the luminiferous ether in their neighbourhood becomes disturbed, and waves are produced, which, if of certain wave-lengths, are capable of detection as light. The longer waves are termed non-luminous thermal radiations.

Non-Luminous Radiations possess the general properties of light waves, being capable of reflection, refraction, polarization, &c. If light waves are absorbed, heat is produced in the absorbing body. A similar production of heat attends the absorption of non-luminous radiations.

Diathermancy is the name given to the degree of transparency of a substance, with respect to thermal radiations. Substances which absorb thermal radiations are said to be *athermanous.*

Air, oxygen, nitrogen, and hydrogen are almost transparent to thermal radiations. If this were not the case, hardly any heat could reach the earth from the sun.

Theory of Exchanges. Any body, not at the absolute zero of temperature, emits radiations. In a state of thermal equilibrium, the amount of energy radiated per second from a body is equal to the energy absorbed by it in the form of radiations from surrounding bodies.

The Emissivity of a surface is equal to the net amount of energy radiated from unit area of the surface in one second, per unit difference of temperature between the surface and surrounding bodies.

The Pyro-heliometer is an instrument for determining the energy radiated from the sun which falls on unit area of a body on the earth. From a knowledge of the above quantity, together with the assumption of some law of cooling at high temperatures, the temperature of the sun may be estimated.

QUESTIONS ON CHAPTER XXI.

(1) Describe the details of an experiment to investigate the laws of the refraction of non-luminous radiation.

(2) Describe carefully experiments which have been made on the absorption of heat by vapours, dealing specially with the error which may arise through the absorption of heat by films of liquid through which the radiation passes.

(3) Describe convenient apparatus for investigating the laws of the reflection and refraction of non-luminous radiations, and give the general results which have been arrived at.

(4) Describe in detail experiments to prove that bodies transparent to light may absorb invisible radiations in very different degrees.

(5) State Prevost's theory of exchanges, and show how it follows from the theory that the radiating and absorbing powers of a surface at a given temperature are the same.

(6) Describe the most important experimental results on the absorption of radiation by gases.

(7) How would you propose to determine the quantity of radiant heat received from the sun on a square inch on the earth's surface?

(8) What is meant by the theory of exchanges?

Account for the fact that good radiators are also good absorbers.

(9) Describe any method by which the rate of radiation received from the sun has been determined. State briefly the reasons for the conclusion that all the radiation measured is of one kind, differing only in wave-length.

(10) State Prevost's theory of exchanges. Describe and discuss experiments which illustrate it.

(11) Describe experiments which have been made to determine the law of radiation from heated surfaces.

Give an account of some method by which it has been sought to measure the temperature of the radiating surface of the sun.

(12) A wire ·1 cm. in diameter, carrying a current of 10 ampères, is found to reach a steady temperature of 100° C. Assuming the specific resistance of the material as $2{\cdot}1 \times 10^{-4}$ ohms per cm. cube, and the value of J as 42×10^6 ergs, determine the amount of heat emitted at 100° C. by a square centimetre of the surface.

PRACTICAL.

(1) Given a Leslie cube, a thermopile, and a galvanometer, find the relation between the radiation from the cube, and the excess of temperature above the surroundings.

(2) Measure and plot the radiation of a tin of boiling water at different distances from a given thermopile.

(3) Compare the radiating powers of two given surfaces by means of a thermopile.

MISCELLANEOUS EXAMPLES

(1) Show in a general manner that according to the kinetic theory of gases the pressure is proportional to the mean kinetic energy of agitation, and establish Avogadro's law as a consequence of the theory.

(2) Show how to obtain the gaseous laws of Boyle, Charles, and Avogadro from the principles of the kinetic theory of gases.

(3) Obtain a formula giving the value of J in terms of the pressure, temperature, and density of a mass of gas, and the difference between its two specific heats. What experiments are necessary to justify the assumption made in obtaining the formula?

(4) Explain how the thermal equivalent of mechanical energy may be derived from a knowledge of how much heat is required to warm a given quantity of gas a given number of degrees, first when pressure on it is kept constant, and next when it is heated in a closed inexpansible vessel.

(5) What is meant by an isothermal curve? Indicate the form of such a curve (1) for a gas, (2) for a vapour, tracing the curve in the latter case from the condition of unsaturated vapour to that of complete liquefaction, and explain how the work done in compressing the gas or vapour may be represented in either case.

(6) Define the terms work, force, pressure. Show that if a piston is moved along a cylinder against a constant pressure, the work done in a stroke is equal to the product of the pressure into the volume swept out by the piston. Explain clearly the units in which the work will be given by this calculation.

(7) Prove that the ratio of the two specific heats of a gas at constant pressure and volume respectively is the same as the ratio of its adiabatic and thermal elasticities.

(8) Find the equation of an adiabatic of a refractory gas, such as air.

(9) What are the properties which determine the velocity of sound in a solid, a liquid, or a gas? Explain why Newton's value of the velocity of sound in air differs from the true value. Calculate the Newtonian velocity of sound in a gas whose density at standard pressure and

temperature is 1 kilogram per cubic metre. What would you expect the true velocity to be?

(10) If a quantity of air at 15° C. is suddenly compressed to half its volume, show how to calculate the temperature it will momentarily attain. Explain the importance of this knowledge in the theory of sound propagation.

(11) What effect does pumping half the air out of a closed vessel produce on the velocity of sound passing through it? Also, what is the effect of compressing the air? (The temperature in both cases is supposed to be constant.)

(12) The specific gravity of a certain gas, under a pressure of 75 cms. of mercury at 0° C., is one-thousandth that of water. What is the velocity of sound in it at that temperature? What is it also at the temperature 100°? Examine whether altering the pressure on the gas will affect the velocity. (Take the ratio of the two specific heats as 1·4.)

(13) How does the velocity of sound through different gases at the same temperature and pressure depend upon the density of the gas? Describe a simple experiment by which you could prove that the velocity of sound through coal-gas is not the same as the velocity through air.

(14) Describe the various methods employed to determine the ratio of the specific heats of gases. What inference as to the constitution of the molecule of the gas is sometimes drawn from these measurements?

(15) Explain the possibility of the artificial production of cold by the performance of mechanical work on a suitable substance. If ordinary dry air at ten atmospheres is suddenly released, explain how the reduction of temperatures can be calculated.

(16) What is meant by the statement that the specific heat of saturated steam at 100° is negative?

Assuming that steam obeys the gas laws, show that the work done in changing the volume of 1 gram of steam at 100° and 760 mm. to the volume of 101° and 787 mm. (the saturation pressure at 101°), is more than sufficient to supply the heat needed for the rise in temperature, the specific volume of steam at 100 being taken at 1,700, and its specific heat at constant pressure as 0·48.

(17) A cylindrical calorimeter, outside diameter 20 cms., is suspended by a single wire so that it is capable of rotation about its axis, which is vertical. A paddle is rotated within the calorimeter at the rate of 1,500 turns per minute, and the calorimeter is kept from rotating by means of two fine strings which are wound round the outside of the calorimeter on opposite sides and then pass over two pulleys and have each a weight of 200 grams attached. If the mechanical equivalent of heat is $4·189 \times 10^7$, and g is 981, find the heat (in gram-calories) developed in the calorimeter in each second.

(18) If we take v in the equation of an ideal gas, $pv = \mathrm{RT}$, to be the volume of m grams of a gas of which the molecular weight is m, show that R is the same for all gases, and find its value in C.G.S. units, given that the density of hydrogen at 0° C. and a pressure of one megadyne [10^6 dynes] per sq. cm. is 0·0896 grams per litre.

(19) Describe Victor Meyer's method of measuring vapour density.

An experiment made by this method gave the following numbers. Calculate the vapour density of the substance :—

Weight of liquid = 0·119 gram.

Volume of air driven off (collected over mercury) = 38 c.c.

Temperature of air = 15° C.

Height of the mercury surface inside the measuring tube above the free surface = 5 cms.

Height of the barometer = 75 cms.

(20) By what processes does hot water standing in an open vessel lose heat? Describe experiments by which the existence of the several causes of loss can be determined.

(21) A glass bulb of 100 c.c. capacity is connected to a vertical tube 3 mm. in diameter dipping in a dish of mercury. The mercury stands at the top of the tube at a height of 30 cms., when the bulb is at 0° C. When the bulb and tube are surrounded by steam at atmospheric pressure of 760 mm., the mercury is observed to fall to 14 cms Find the coefficient of dilatation of the gas in the bulb, neglecting the expansion of the glass.

(22) Define the thermal conductivity of a substance. A glass vessel with an area of 100 sq. cms., 1·5 mm. thick, is filled with ice and placed in a vessel kept at a temperature of 100° C. Find how many grams of ice will melt per minute when the flow of heat has become steady

Latent heat of ice = 80.

Conductivity of glass = 0 00185 *c.g.s.*

(23) Find the efficiency of an air engine using one pound of coal per horse-power hour, and compare it with that of a perfect reversible engine, assuming that the heater is at 1,000° C., and the refrigerator at 0° C., and that the thermal value of the coal is 8,000 calories per gram.

(24) A piece of sulphur weighs 50 grams in air, and has a volume of 25 c.c., when the temperature is 17° C. and pressure 74 cms. What is its true weight, the density of air being 0·00129 grm. per c.c., at 0° and 76 cms., the coefficient of expansion of air 1/273, and the density of the brass weights 8·0 grms. per c.c.?

(25) A glass globe contains unsaturated moist air, and the pressure is so adjusted that on opening a stop-cock communicating with th

external air, a very slight cloudiness is produced. Show that, if the initial and final pressures of the air and its hygrometric state are known, we can calculate the ratio of the specific heats for the moist air.

(26) Explain the cause of draught in chimneys. What average excess in temperature, in a chimney 136 feet high, would in ordinary circumstances produce a pull measured by 1 inch on the water gauge?

(27) A thoroughly jacketed vessel contains a liquid in which a spiral of wire is immersed. An E.M.F. of 20 volts is applied to the ends of the spiral, and a current of 2 amperes passes through it. Five grams of the liquid are boiled away every minute after steady boiling has begun. What is the latent heat of vaporisation of the liquid?

(28) A watch has a non-compensated brass balance wheel and a steel balance spring. How many seconds will it lose per day for 1° rise of temperature if the coefficient of linear expansion of brass is $18 \div 10^6$, and if Young's modulos for steel at t° is

$$2 \times 10^{12}\left(1 - \frac{2t}{10^4}\right)?$$

(29) Find the number of watts in one Horse Power, given 1 foot = 30·48 cm. : 1 lb. = 453·6 gms. : $g = 981$ cm./sec.^{2}.

Electrical energy is sold at the rate of 4*d.* per kilowatt-hour. The mechanical equivalent of the heat given by the burning of coal worth 4*d.* is 10^8 foot-lbs. Compare the prices of the two forms of energy. Why is electrical energy so much dearer than coal energy?

(30) A closed porous pot filled with air is provided with a manometer. Describe what are the indications of the manometer if the pot is suddenly surrounded by and kept in (*a*) coal gas, (*b*) carbonic acid.

Give some explanation on the Kinetic Theory.

(31) A tuning fork gives a particular note at 15°. It is put in boiling water, and immediately after it is taken out its frequency is lowered one per cent. The coefficient of linear expansion of the metal is $12 \div 10^6$. What is the temperature change in the elastic constant?

(32) Describe and discuss the experiments of Joule and Thomson on the flow of gases through a porous plug.

What bearing has the Joule-Thomson effect on the methods now used for liquefying gases?

(33) Enumerate the principal corrections to be applied to the reading of a mercury thermometer, and indicate briefly the manner in which they may be determined. What will be the reading of an accurate mercury thermometer if the bulb is at 300° C., and the stem from 0° upwards at 20° C.? The coefficient of expansion of mercury may be taken as 0·000187, and the linear coefficient of glass 0·0000090.

(34) Explain carefully the method of determining the pressure-

coefficient of a gas by means of the constant-volume thermometer. If, in this method, one per cent. of the volume of the gas is exposed to a temperature of 20° C. throughout the observations, find what correction must be applied to the pressures observed at 0° and 100° C.

(35) Describe how you would determine the specific heat of ice and its latent heat of fusion. What are the principal precautions required for obtaining an accurate result?

(36) The volume of a gas is suddenly increased by one per cent., and the immediate fall of pressure is observed. The gas is then raised to its original temperature at constant volume, and the increase of pressure measured. Show how to find the ratio of the specific heats from these observations.

(37) State Newton's law of cooling, and explain its limitations. How can it be reconciled with the law that the radiation from a black body varies as the fourth power of the absolute temperature?

(38) Draw a diagram showing the general form of the isothermals, including both liquid and vapour, and explain which portions of the diagram correspond to liquid, saturated vapour, and coexistence of liquid and saturated vapour.

What evidence is there for the idea that the true form of the part of the isothermal corresponding to the coexistence of liquid and vapour is not a straight line?

(39) Describe, illustrating your answer by a diagram, exactly what happens when a solution of common salt is cooled from 0° C. to such a temperature that the whole solidifies.

(40) Explain how the real coefficient of expansion of mercury has been determined.

(41) What is meant by the hygrometric state of the air?

Describe how the dew-point can be measured, and show that knowing the dew-point and the temperature of the air we can calculate the hygrometric state.

(42) Discuss the relative advantages of thermo-electric and platinum-resistance methods for different kinds of temperature measurement.

(43) How is the validity of Dulong and Petit's law of atomic heat affected by the variation of specific heat with temperature and by the state of aggregation of the element considered?

(44) Describe a continuous process of liquefying air. What special difficulties are encountered in the application of the method to hydrogen?

(45) Give some account of recent investigations of the mechanical equivalent of heat, excluding electrical methods.

(46) Explain the principle of Fairbairn and Tate's method of measuring the density of saturated steam. Criticise the method carefully, and

explain how the density may be deduced theoretically from other measurements.

(47) If the thermal conductivity of ice is 0·0050 C.G.S., find the rate at which the ice on a pond will increase in thickness if the air in contact with upper surface of the ice is maintained by radiation, &c., at a temperature of 20° below zero C. Plot a curve showing how the rate varies as the thickness of the ice increases.

(48) A metal ball at a temperature of t_0° C. is placed in the middle of an enclosure, of which the walls are maintained at 0° C.; six minutes afterwards the temperature of the ball is 300° C., and after another minute it is 250° C. Find the value of t_0, assuming Newton's law of cooling.

(49) Show how the rise in temperature when a gas is forced through a porous plug may, by use of the second law of thermodynamics, be applied to determine the absolute zero.

(50) Calculate the work done during adiabatic expansion to infinity of a given mass of gas which is initially under standard conditions of temperature and pressure.

APPENDIX

THE WET AND DRY BULB HYGROMETER.

This table gives the pressure, in mm. of mercury, that would be exerted by the aqueous vapour in the atmosphere when cooled to the dew point; the dry bulb reading being t° C, and the difference between the dry and wet bulb readings being equal to the respective numbers in the top line.

(Compiled from Table 170, Smithsonian Physical Tables.)

t° C.	0	1	2	3	4	5	6	7	8	9	10
0	4·6	3·7	2·9	2·1	1·3	...	...	...	...	...	...
1	4·9	4·1	3·2	2·4	1·6	...	...	...	...	...	...
2	5·3	4·4	3·6	2·7	1·9	1·1	0·3	...	...	...	...
3	5·7	4·8	3·9	3·1	2·2	1·4	0·6	...	...	...	...
4	6·1	5·2	4·3	3·4	2·6	1·8	0·9	...	...	...	...
5	6·5	5·6	4·7	3·8	2·9	2·1	1·2	...	...	...	...
6	7·0	6·0	5·1	4·2	3·3	2·4	1·6	...	...	...	...
7	7·5	6·5	5·5	4·6	3·7	2·8	1·9	1·1	0·2	...	...
8	8·0	7·0	6·0	5·0	4·1	3·2	2·3	1·4	0·6	...	...
9	8·6	7·5	6·5	5·5	4·5	3·6	2·7	1·8	0·9	...	...
10	9·2	8·1	7·0	6·0	5·0	4·0	3·1	2·2	1·3	...	...
11	9·8	8·7	7·6	6·5	5·5	4·5	3·5	2·6	1·7	...	..
12	10·5	9·3	8·2	7·1	6·0	5·0	4·0	3·0	2·1	1·2	0·3
13	11·2	10·0	8·9	7·6	6·5	5·5	4.5	3·5	2·5	1·6	0·7
14	11·9	10·7	9·4	8·3	7·1	6·1	5·0	4·0	3·0	2·0	1·1
15	12·7	11·4	10·1	9·0	7·8	6·6	5·5	4·5	3·4	2·5	1·5
16	13·5	12·2	10·9	9·7	8·4	7·3	6·0	5·0	4·0	3·0	1·9
17	14·4	13·0	11·7	10·4	9·1	8·0	6·7	5·6	4·5	3·5	2·4
18	15·4	13·9	12·5	11·2	9·9	8·6	7·4	6·3	5·1	4·0	3·0
19	16·3	14·9	13·4	12·0	0·7	9·4	8·1	6·9	5·7	4·6	3·5
20	17·4	15·9	14·3	12·9	11·5	10·2	8·8	7·6	6·4	5·2	4·1
21	18·5	16·9	15·3	13·8	12·4	11·0	9·6	8·4	7·1	5·9	4·7
22	19·7	18·0	16·4	14·8	13·3	11·9	10·5	9·1	7·8	6·6	5·4
23	20·9	19·2	17·5	15·9	14·3	12·8	11·3	10·0	8·6	7·3	6·1
24	22·2	20·4	18·6	17·0	15·3	13·8	12·3	10·9	9·4	8·1	6·8
25	23·5	21·7	19·9	18·1	16·4	14·8	13·3	11·8	10·3	9·0	7·6
26	25·0	23·1	21·1	19·4	17·6	15·9	14·3	12·8	11·3	9·8	8·4
27	26·5	24·5	22·5	20·7	18·8	17·1	15·4	13·8	12·3	10·6	9·3
28	28·1	26·0	24·0	22·0	20·1	18·3	16·6	14·9	13·3	11·8	10·2
29	29·8	27·6	25·5	23·5	21·5	19·6	17·8	16·1	14·4	12·8	11·2
30	31·5	29·3	27·1	25·0	22·9	21·0	19·1	17·3	15·5	13·9	32·3

MAXIMUM PRESSURE OF AQUEOUS VAPOUR AT DIFFERENT TEMPERATURES.

Deduced by Broch from Regnault's Experimental Data.
(The pressure *p* is given in mm. of mercury, at 0° C, and at the sea level in lat. 45°.)

Temp. °C.	*p*.	Temp. °C.	*p*.	Temp. °C.	*p*.	Temp. °C.	*p*
0	4·57	26	24·96	51	96·66	76	301·09
1	4·91	27	26·47	52	101·55	77	313·85
2	5·27	28	28·07	53	106·65	78	327·05
3	5·66	29	29·74	54	111·97	79	340·73
4	6·07	30	31·51	55	117·52	80	354·87
5	6·51	31	33·37	56	123·29	81	369·51
6	6·97	32	35·32	57	129·31	82	384·64
7	7·47	33	37·37	58	135·58	83	400·29
8	7·99	34	39·52	59	142·10	84	416·47
9	8·55	35	41·78	60	148·88	85	433·19
10	9·14	36	44·16	61	155·95	86	450·47
11	9·77	37	46·65	62	163·29	87	468·32
12	10·43	38	49·26	63	170·92	88	486·76
13	11·14	39	52·00	64	178·86	89	505·81
14	11·88	40	54·87	65	187·10	90	525·47
15	12·67	41	57·87	66	195·67	91	545·77
16	13·51	42	61·02	67	204·56	92	566·71
17	14·40	43	64·31	68	213·79	93	588·33
18	15·33	44	67·76	69	223·37	94	610·64
19	16·32	45	71·36	70	233·31	95	633·66
20	17·36	46	75·13	71	243·62	96	657·40
21	18·47	47	79·07	72	254·30	97	681·88
22	19·63	48	83·19	73	265·38	98	707·13
23	20·86	49	87·49	74	276·87	99	733·16
24	22·15	50	91·98	75	288·76	100	760·00
25	23·52					101	787·67

VOLUME, IN C.CS., OCCUPIED BY 1 GRAM OF WATER AT VARIOUS TEMPERATURES (*Rosetti*).

Temp. °C.	Vol. c.cs.	Temp. °C.	Vol. c.cs.	Temp. °C.	Vol. c.cs.	Temp. °C.	Vol. c.cs.
−10	1·00186	8	1·00011	26	1·00314	44	1·00929
− 9	1·00157	9	1·00018	27	1·00341	45	1·00971
− 8	1·00132	10	1·00025	28	1·00368	46	1·01014
− 7	1·00109	11	1·00034	29	1·00396	47	1·01057
− 6	1·00088	12	1·00045	30	1·00425	48	1·01101
− 5	1·00070	13	1·00057	31	1·00455	49	1·01148
− 4	1·00054	14	1·00070	32	1·00486	50	1·01195
− 3	1·00041	15	1·00084	33	1·00518		
− 2	1·00030	16	1·00100	34	1·00551	55	1·01439
− 1	1·00020	17	1·00116	35	1·00586	60	1·01691
0	1·00013	18	1·00135	36	1·00621	65	1·01964
1	1·00007	19	1·00154	37	1·00657	70	1·02256
2	1·00003	20	1·00174	38	1·00694	75	1·02566
3	1·00001	21	1·00196	39	1·00732	80	1·02887
4	1·00000	22	1·00218	40	1·00770	85	1·03221
5	1·00001	23	1·00240	41	1·00809	90	1·03567
6	1·00003	24	1·00264	42	1·00849	95	1·03931
7	1·00007	25	1·00289	43	1·00889	100	1·04312

PROPERTIES OF STEAM (*Callendar*).

See *Proc. Roy. Soc.*, Vol. 67 (1900), pp. 226–286.

Temp. C.	V.	P.	Q.	L.	S.	Entropy.	
						Water.	Steam.
0	202,602·0	4·66	593·5	593·5	−1·680	0	2·1740
20	57,309·0	17·67	603·3	583·2	−1·502	0·07087	2·0617
40	19,442·0	55·55	613·0	573·0	−1·351	0·13681	1·9676
60	7,671·0	149·63	622·5	562·5	−1·223	0·19868	1·8880
80	3,407·0	355·30	631·7	551·7	−1·116	0·25704	1·8198
100	1,672·5	760·00	640·3	540·2	−1·028	0·31246	1·7608
120	890·6	1,491·4	648·4	528·1	−0·955	0·36518	1·7090
140	508·4	2,716·5	655·8	515·2	−0·895	0·41567	1·6632
160	307·1	4,657·0	662·4	501·3	−0·844	0·46373	1·6215
180	195·3	7,546·0	668·4	486·8	−0·801	0·51029	1·5849
200	129·6	11,684·0	673·4	471·1	−0·759	0·55492	1·5509

In the above table, the unit of heat employed is that required to raise 1 gram of water through 1° C. at 20° C. (See p. 135.)

V.=Specific Volume (volume in cc.s., of 1 gram) of saturated steam.
P.=Pressure, in mm. of mercury, of saturated steam.
Q.=Total Heat of Steam. } See p. 153.
L.=Latent Heat of Steam. }
S.=Specific heat of saturated steam. (See p. 330.)

ANSWERS TO QUESTIONS

CHAPTER I

(2) 20° C., 80° C., −28·9° C., 39·5° F., 125·6° F., −459·4° F.
(5) 36·95° C., 89·32° C.

CHAPTER II

(6) 99·65° C.

CHAPTER III

(3) +0·029 cm.
(5) 0·051 cm.
(6) 14·69 ins.
(7) 22·1 cms.
(8) ·99496 c.ft.
(10) 0·12 of one per cent.

CHAPTER IV

(2) 6·0667 grams.
(3) 0·139, or, roughly, $\frac{1}{7}$ of the whole volume of glass vessel.
(4) 0·000061.
(11) Let g = coefficient of linear expansion of glass.
,, r = internal radius of glass tube. Then

$$\pi\{r(1+100g)\}^2 \times 101{\cdot}65 = \pi r^2 \times 100 \times 1{\cdot}0182 \text{ (see p. 65).}$$

$$\therefore\ (1+2\times 100g)\times 101{\cdot}65 = 101{\cdot}82 \text{ (see p. 52).}$$

$$g = 0{\cdot}0000083.$$

∴ Coefficient of cubical expansion of glass = 0·0000249.
(12) 288°.

CHAPTER V

(2) 29·45 ins.
(3) 0·00366.
(9) Take density of dry air, at 0° C. and 760 mm. pressure, equal to 0·001293 gr./c.c. Work performed = $1{\cdot}29 \times 10^8$ ergs.
(16) 999·3 grams per sq. cm.
(18) 30 ins.
(19) 452° C.

CHAPTER VI

(6) 0·497.
(8) 0·0911.
(10) 0·489.
(11) 0·14.
(12) 9660 heat units.
(14) Water equivalent = 12. Specific heat of metal = 0·112.

CHAPTER VII

(7) 7962·5 grams of ice.
(8) 0·11.
(11) Time to commencement of freezing : time to freezing of hal inch = 40 : 61.
(12) 630.

CHAPTER VIII

(5) 0·103.
(9) Use formula on p. 372. Melting point raised by 0·025° C.

CHAPTER X

(10) 0·745.
(14) 0·3424 grams.
(15) $\frac{8}{780}$.
(17) At 30°, vapour pressure = 30·56 cms. of mercury.
,, 45°, ,, ,, = 49·71 ,, ,, ,,
,, 60°, ,, ,, = 81·87 ,, ,, ,,

CHAPTER XI

(2) $1{\cdot}0296 \times 10^9$ ft.-lbs.; 52 horse-power.

CHAPTER XII

(1) $8{\cdot}0 \times 10^5$ cms.
(2) $2{\cdot}98 \times 10^6$ heat units.
(3) 132,000 B.T.U. One British Thermal Unit (B.Th.U.) = the heat required to raise 1 lb. of water through 1° F.
(5) $3{\cdot}45 \times 10^4$ cms. per sec.
(6) 0·1972 heat units, where 1 heat unit would raise 1 lb. of water through 1° C.
(11) $41{\cdot}2 \times 10^3$ ergs. per therm.
(13) $\frac{1}{8}$.

CHAPTER XV

(1) 213° C. This problem can be solved like that on p. 320. If no logarithms are given, we can proceed as follows:

$$\frac{T_1}{T_0} = \left(\frac{v_0}{v_1}\right)^{\gamma-1} = (4)^{\cdot 4} = (4)^{\frac{2}{5}} = (2^4)^{\frac{1}{5}} = \left(\frac{2^5}{2}\right)^{\frac{1}{5}} = 2(\tfrac{1}{2})^{\frac{1}{5}} = 2(1-\tfrac{1}{2})^{\frac{1}{5}}.$$

We can now expand $(1-\frac{1}{2})^{\frac{1}{5}}$ by the Binomial Theorem.

CHAPTER XVI

(7) 0·26, or 26 per cent.

(8) $1\frac{1}{8}$.

CHAPTER XVII

(3) 496·2 heat units.

CHAPTER XVIII

(6) 1·17° C.

CHAPTER XX

(4) 21,600.

(6) 1,800,000 grams of ice.

(7) 1·79° C.

(10) $1{\cdot}26 \times 10^{-5}$.

CHAPTER XXI

(12) 2·03 therms per sq. cm.

MISCELLANEOUS EXAMPLES

(6) If pressure is measured in dynes per sq. cm., and the volume in c.cms., work will be measured in ergs. If pressure is measured in grams per sq. cm., and volume in c.cms., work will be measured in cm-grams. If pressure is measured in lbs. per sq. ft. and volume in c.ft., work will be measured in ft.-lbs.

(9) Newtonian Velocity of sound = $3{\cdot}17 \times 10^4$ cms. per sec.

(12) Velocity = $3{\cdot}74 \times 10^4$ cms. per sec. at 0°,
and $4{\cdot}37 \times 10^4$,, ,, ,, ,, 100°.

(16) Diminution of volume = 54 c.cs.

Average pressure = 773 mm. of mercury = $1{\cdot}03 \times 10^6$ dynes per sq. cm. Work done during compression is equivalent to 1·32 therms.

(17) 14·7 gram-calories per second.

(18) Molecular weight of hydrogen = 2. Volume of 2 grams of hydrogen at 0° C. and 76 cms. pressure,

$$= \frac{2 \times 1{,}000}{0{\cdot}0896} = 22{,}320 \text{ c.c}$$

$$R = \frac{10^6 \times 22{,}320}{273} = 8{\cdot}176 \times 10^7.$$

(19) If the vapour obeyed the gas laws, its density, at 0° C. and 76 cms. pressure, would be—

$$\frac{0{\cdot}119 \times 76 \times 288}{38 \times 70 \times 273} = 0{\cdot}03586 \text{ grm. per c.c.}$$

(21) Use equation $pv = k(1 + at)$—

When $t = 0°$ C., $p = 46$, and $v = 100$. $\therefore\ k = 4{,}600$.

Then, at 100° C., $62 \times 101{\cdot}13 = 4{,}600\,(1 + 100\,a)$—

$$a = 0{\cdot}00363,$$

neglecting the expansion of the glass, and the diminished density of the mercury, at 100° C.

(22) 92·5 grms. per minute.

(23) Heat liberated by coal $= 8{,}000 \times 454$ calories per horse-power hour $= 3{\cdot}63 \times 10^6$.

1 H.P. $= 746 \times 10^7$ ergs per second. Heat equivalent of 1 H.P. hour

$$= \frac{746 \times 10^7 \times 3{,}600}{42 \times 10^6} \text{ calories.}$$

$$\text{Actual efficiency} = \frac{7{\cdot}46 \times 3{\cdot}6 \times 10^{12}}{4{\cdot}2 \times 10^7} \div (3{\cdot}63 \times 10^6) = 0{\cdot}17.$$

Efficiency of perfect reversible engine working between temperatures 1,000° C. and 0° C. $= \frac{1{,}000}{1{,}273} = 0{\cdot}78$.

(24) Mass of air displaced by sulphur—

$$= \frac{25 \times 74 \times 273}{76 \times 290} \times 0{\cdot}00129 = 0{\cdot}0296 \text{ grams.}$$

Since density of weights = 8, while density of sulphur = 50/25 = 2, the weights displace one-quarter of the mass of air displaced by sulphur, *i.e.* 0·0074 grams.

$\therefore$ True mass of sulphur $= 50 + 0{\cdot}0296 - 0{\cdot}0074 = 50{\cdot}0222$ grams.

(26) Mass of heated air in chimney must be less than that of similar column at atmospheric temperature by mass of cylinder of water 1 inch in height, and of same sectional area as the chimney. Thus if a sq. ft. = sectional area of chimney, d_1 = density of hot gases in chimney at an absolute temperature T, and d = density of surrounding air at 15° C. (say), or 288° abs., we have

$$136(d - d_1)a = \frac{62}{12} \times a \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1),$$

the density of water being 62 lbs. per cubic foot.

Also, density of gas within chimney will not be appreciably affected by the difference in its pressure from that of the surrounding air. Thus, if d_0 = density of air at 0° C. (273° abs.),

$$d = \frac{273}{288}d_0, \text{ and } d_1 = \frac{273}{T}d_0.$$

Thus for (1)

$$136 \times 273 \times d_0\left(\frac{1}{288} - \frac{1}{T}\right) = \frac{62}{12} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The density, d_0, of atmospheric air at 0° C. and standard barometric pressure is 0·0809 lb. per cubic foot. In the above we have assumed that the flue gases at 0° and under standard barometric pressure would have the same density as the air, although they would really be somewhat denser. Substituting for d_0 in (2), and solving for T, we obtain

$$T = 572° \text{ (nearly)}$$

$\therefore$ 572 − 288 = 284° C. = excess of temperature required.

(27) Heat dissipated by electric current = $(20 \times 2 \times 10^7) \div (42 \times 10^6)$ = 9·52 gram-calories (or therms) per second, or 9·52 × 60 = 571·2 therms per minute.

$\therefore$ Latent heat of liquid 571·2 ÷ 4 = 142·8 therms per gram.

(28) The time of vibration of a balance wheel varies as $\sqrt{I/Y}$, where I is the moment of inertia of the wheel, and Y is the Young's modulus of the hair-spring. Now a rise of temperature will cause the linear dimensions of the wheel to increase, and I will vary directly as the square of the linear dimensions; thus

$$\frac{\text{Time of vibration at } (t+1)°}{\text{Time of vibration at } t°} = \left\{\sqrt{\frac{I(1 + 18 \times 10^{-6})^2}{Y(1 - 2 \times 10^{-4})}} \div \sqrt{\frac{I}{Y}}\right\}$$

$$= \frac{1 + 18 \times 10^{-6}}{\sqrt{1 - 2 \times 10^{-4}}}.$$

Number of seconds lost per day due to 1° rise of temperature = 10·2.

(29) 1 H.P. = 746 watts.

1 kilowatt hour = 1·34 H.P. hour = 1·34 × 33,000 × 60 ft. lbs. = $2·66 \times 10^6$ ft. lbs.

$2·66 \times 10^6$ ft. lbs. of electrical energy cost 4*d.*

10^8 ft. lbs. of heat energy (in coal) cost 4*d.*

$\therefore$ Cost of electrical energy : cost of heat energy in coal = 100 : 2·66.

It is only possible to convert a small proportion of the heat in coal into mechanical energy. See Chapter XVI.

The cost of labour and interest on the value of plant used in converting heat energy into mechanical energy must also be taken into account.

(31) The frequency of vibration of a tuning fork (that is, the number of vibrations it performs per second) varies directly as $\sqrt{Y/d}$, where Y is the Young's modulus of the steel, and d is its density. Heating the fork to 100° C. (*i.e.*, through 85° C) diminishes the density of the steel in the ratio $1 : (1 + 12 \times 85 \times 10^{-6})^3 = 1 : (1{\cdot}00102)^3 = 1 : 1{\cdot}0031$. Let y be the temperature coefficient of the Young's modulus of the steel; thus

$$\frac{\text{Frequency at } 100^\circ}{\text{Frequency at } 15^\circ} = \frac{99}{100} = \sqrt{(1 + 85v) \times 1{\cdot}0031}.$$

$$\therefore\ 1 + 85y = \left(\frac{99}{100}\right)^2 \div 1{\cdot}0031$$

$$= \frac{0{\cdot}98}{1{\cdot}0031} = 0{\cdot}977.$$

$$\therefore\ y = -\ {\cdot}023 \div 85 = 2{\cdot}7 \times 10^{-4}.$$

(33) 287·1° C.

(34) *a. Bulb at* 0° C.—Let V be the total volume of the bulb and connecting tube, supposed to be constant; while v is the volume of the connecting tube, kept at 20° C. Let P_0 be the observed pressure. If we were to keep the pressure constant, and to cool the gas in the connecting tube down to 0°, the volume of this gas would diminish to $v/(1 + 20\alpha)$ where α is the coefficient of expansion of the gas at constant pressure. In this case the total volume of the gas would be

$$V - v + \frac{v}{1 + 20\alpha} = V - \frac{20\alpha v}{1 + 20\alpha}.$$

If we now decrease the pressure so as to allow the gas to expand at constant temperature to its original volume V, the required pressure P_0' will be given by the equation

$$P_0'V = P_0\left(V - \frac{20\alpha v}{1 + 20\alpha}\right)$$

$$= P_0V\left(1 - \frac{20\alpha v}{(1 + 20\alpha)V}\right).$$

Dividing through by V, the corrected pressure P_0' is given by the equation

$$P_0' = P_0\left(1 - \frac{20\alpha v}{(1 + 20\alpha)V}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We may assume α to be equal to 1/273. In the problem $v/V = 1/100$

$$\therefore\ P'_0 = P_0(1 - 0{\cdot}00069).$$

b. Bulb at 100° C.—Keeping the pressure constant, heat up the connecting tube till its contents are at 100° C.; the volume of the contents will then be equal to $v\,(1 + 100\alpha)/(1 + 20\alpha)$. Then total volume of gas

$$= V - v + \frac{v(1 + 100\alpha)}{1 + 20\alpha} = V + \frac{80\alpha v}{1 + 20\alpha}$$

Let P_1 be the observed pressure, and P_1' the required corrected pressure; then if we compress the gas at constant temperature until its volume is equal to V, we have

$$P_1'V = P_1\left(V + \frac{80\alpha v}{1 + 20\alpha}\right)$$

$$= P_1V\left(1 + \frac{80\alpha v}{(1 + 20\alpha)V}\right)$$

$$\therefore\ P_1' = P_1\left(1 + \frac{80\alpha v}{(1 + 20\alpha)V}\right) = P_1(1 + 0{\cdot}00273).$$

(37) Heat radiated from body $= kT_1^4$, where T_1 is the absolute temperature of the body. Heat received by body from surroundings $= kT_0^4$, where T_0 is the absolute temperature of surroundings. Then net loss of heat $= k(T_1^4 - T_0^4) = k(T_1 - T_0)\,(T_1^3 + T_1^2T_0 + T_1T_0^2 + T_0^3)$.

With a moderate difference of temperature between a body and its surroundings, the value of the expression just found will be directly proportional to $(T_1 - T_0)$, and small variations in T_1 and T_0 will not greatly influence the quantity within the second set of brackets.

(47) A complete solution of this problem would be difficult to obtain without the use of the higher mathematics; the following approximate solution is probably what the examiner desired.

When a layer of ice is first formed, its temperature is 0° C.; when an additional layer is formed, the temperature of the first layer must fall, otherwise heat would not pass into it from the layer last formed. Hence the heat passing through the ice is really made up of two parts, one due to the latent heat given up by the ice in freezing, and the other due to the heat given up during the cooling of the various layers of ice. The specific heat of ice is equal to 0·5, while its latent heat is equal to 80 gram-calories per gram. Hence we may, to a first approximation, neglect the heat given up by the ice as it cools; the error involved will not be considerable unless the ice is very thick.

Let K = thermal conductivity of ice; then K = quantity of heat passing normally through a square centimetre per second, ÷ temperature gradient. Under the conditions specified above, the temperature gradient may be considered uniform throughout the ice, its value being

20° ÷ thickness of ice, supposing the water in the pond to be at a temperature of 0° C.

At a given instant let the thickness of the ice be x_0, the time being t_0. At time t_1 let the thickness of the ice be x_1, the time interval $(t_1 - t_0)$ being very small, and therefore $(x_1 - x_0)$ being small. Then during this interval of time the average thickness of ice $= (x_1 + x_0)/2$, and the average temperature gradient $= 20 \div (x_1 + x_0)/2$. Then if $q =$ the quantity of heat which passes through a square centimetre of the ice in the interval $(t_1 - t_0)$,

$$K = \frac{\dfrac{q}{t_1 - t_0}}{\dfrac{20}{(x_1 + x_0)/2}}$$

$$\therefore q = \frac{40\,K\,(t_1 - t_0)}{x_1 + x_0}.$$

But q is the quantity of heat given up during the formation of a layer of ice one square centimetre in area and $(x_1 - x_0)$ centimetres thick, from water at 0° C. The density of ice being about 0·91, the mass of this layer of ice $= (x_1 - x_0) \times 1 \times 0{\cdot}91$, and in freezing, this mass will give up

$$0{\cdot}91\,(x_1 - x_0) \times 80 = 73\,(x_1 - x_0)$$

heat units. Then

$$q = 73\,(x_1 - x_0) = \frac{40\,K\,(t_1 - t_0)}{x_1 + x_0},$$

$$\therefore x_1^2 - x_0^2 = 0{\cdot}55\,K\,(t_1 - t_0) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

During the next short interval of time $(t_2 - t_1)$ let the ice increase in thickness from x_1 to x_2 centimetres. Thus

$$x_2^2 - x_1^2 = 0{\cdot}55\,K\,(t_2 - t_1) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Similarly

$$x_3^2 - x_2^2 = 0{\cdot}55\,K\,(t_3 - t_2) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$. \quad . \quad . \quad = \quad . \quad . \quad . \quad . \quad . \quad . \quad .$$

$$x_{n-1}^2 - x_{n-2}^2 = 0{\cdot}55\,K\,(t_{n-1} - t_{n-2}). \quad . \quad . \quad (n - 1)$$

$$x_n^2 - x_{n-1}^2 = 0{\cdot}55\,K\,(t_n - t_{n-1}) \quad . \quad . \quad . \quad . \quad (n)$$

Adding together equations (1), (2), (3), ... $(n - 1)$, (n), we obtain

$$x_n^2 - x_0^2 = 0{\cdot}55\,K\,(t_n - t_0).$$

If t_0 represents the time when freezing commences (*i.e.*, $x_0 = 0$), then a layer x centimetres thick will be formed in a time t given by equation

$$x^2 = 0{\cdot}55\,Kt = 0{\cdot}55 \times 0{\cdot}005\,t = 0{\cdot}00275\,t, \text{ and } x = 0{\cdot}052\sqrt{t}.$$

Thus at the end of one second the ice will be 0·052 centimetres thick, at the end of four seconds it will be twice this thickness, &c. The curve representing the connection between x and t is a parabola, with vertex at $t = 0$, $x = 0$, and focus on the axis of t.

(48) According to Newton's law of cooling, the rate at which a body loses heat by radiation is proportional to the difference between its temperature and the temperature of its surroundings; hence, if the specific heat of the body is constant, its rate of fall of temperature is proportional to the difference between its temperature and the temperature of its surroundings.

Let the temperature of the ball at any instant be equal to $t°$ C.; then, since the difference between its temperature and the temperature of its surroundings is $t°$, at the end of a short interval of time its temperature will be equal to $(t - at) = t(1 - a)$, where a is a constant depending only on the length of the short interval of time and the dimensions, mass, and specific heat of the ball. At the end of the next short interval of time, equal to the first interval the temperature will be equal to that at the beginning of this interval multiplied by $(1 - a)$, or $t(1 - a)^2$. If there are n of these intervals in a minute, the temperature at the end of a minute will be equal to $t(1 - a)^n = kt$, where $k = (1 - a)^n$ = a constant depending only on the dimensions, mass, and specific heat of the body. At the end of the second minute the temperature will be equal to k^2t, and at the end of m minutes the temperature will be equal to k^mt. *Hence the temperatures at the ends of equal successive intervals of time form a geometrical progression.*

The initial temperature of the ball being t_0, its temperature at the end of six minutes will be equal to k^6t_0: this is equal to 300° C. After another minute (*i.e.*, at the end of seven minutes) its temperature will be equal to k^7t_0, and this is equal to 250°C. Thus

$$\frac{k^7t_0}{k^6t_0} = k = \frac{250}{300} = \frac{25}{30}.$$

Then, $$k^6t_0 = \left(\frac{25}{30}\right)^6 t_0 = 300;$$

$$\therefore \quad t_0 = 300 \times \left(\frac{30}{25}\right)^6 = 300 \times (1·2)^6.$$

$$= 896° \text{ C.}$$

(49) The solution of this problem involves another, which it will be convenient to deal with first. We shall therefore first prove that **when any substance expands isothermally along a reversible path so**

that the pressure falls from $p + dp$ to p, the heat absorbed by the substance is equal to

$$\frac{\theta}{J} \cdot \frac{\partial v}{\partial \theta} \cdot dp$$

where J = mechanical equivalent of unit quantity of heat.
θ = temperature, measured on thermodynamical scale (p. 345), at which the operation is conducted.
$\frac{\partial v}{\partial \theta}$ = ratio of increase of volume to increase of temperature, when the pressure remains constant.

Let B A (Fig. 1) be a short element of the isothermal of the substance at temperature θ; and let B denote the initial, and A the final, condition of the substance, pressures being measured vertically upwards, and volumes horizontally from left to right. Let D H be an element of the isothermal for a slightly higher temperature $\theta + d\theta$. Draw the adiabatics C A and D B through A and B respectively. Then if a quantity Q of heat is absorbed during the expansion from B to A, and $Q + dQ$ is absorbed during expansion from D to C, it follows (p. 347) that

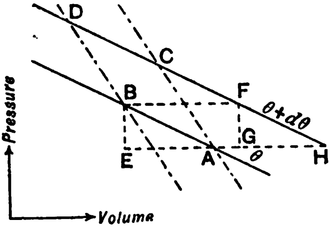

FIG. 1.

$$\frac{Q + dQ}{Q} = \frac{\theta + d\theta}{\theta}$$

$$\therefore \frac{dQ}{Q} = \frac{d\theta}{\theta}, \text{ and } \therefore Q = \theta \frac{dQ}{d\theta}$$

Q is the quantity of heat to be determined. Further, dQ is equal to the area of the cycle D C A B divided by J (p. 338).

To determine area of cycle D C A B, draw the horizontal lines B F and E H through B and A respectively. Through B and F draw the vertical lines B E and F G. Then, areas of parallelograms D C A B and B F H A are equal, since the parallelograms are between the same parallels D H and B A, and have the common base B A. Also, areas of parallelograms B F H A and B F G E are equal, since the parallelograms are between the same parallels B F and E H, and have the common base B F. Therefore areas D C A B and B F G E are equal. Also, B E = dp, the difference between the pressures at B and A. If the rate of increase of volume with temperature when the pressure is constant is equal to $\frac{\partial v}{\partial \theta}$, then $BF = \frac{\partial v}{\partial \theta} \cdot d\theta$.

$$\therefore \text{ Area } DCAB = \text{area } BFGE = BF \times BE = \left(\frac{\partial v}{\partial \theta} \cdot d\theta\right) dp.$$

$$\therefore \frac{dQ}{d\theta} = \frac{1}{J} \frac{\partial v}{\partial \theta} dp,$$

and

$$Q = \theta \frac{dQ}{d\theta} = \frac{\theta}{J} \frac{\partial v}{\partial \theta} dp.$$

Application to a perfect gas. Here $pv = R\theta$, so that

$$v = \frac{R}{p}\theta, \text{ and } \partial v = \frac{R}{p}\partial\theta,$$

$$\therefore Q = \frac{\theta}{J} \cdot \frac{R}{p} \cdot dp = \frac{pv}{Jp} dp = \frac{vdp}{J}.$$

Application to water. Above 4° C., water expands when the temperature rises; that is, $\frac{\partial v}{\partial \theta}$ is positive. Between 0° and 4° C., $\frac{\partial v}{\partial \theta}$ is negative. Therefore, above 4° C., water absorbs heat when it expands isothermally; between 0° and 4° C., water gives out heat when it expands isothermally (*i.e.*, when the pressure to which it is subjected is diminished). The value of $\frac{\partial v}{\partial \theta}$ can be determined from table, p. 470.

Consider, now, the **porous plug experiment.** Let a gram of gas be forced through the porous plug E (Fig. 2) by the piston C, under a pressure $p + dp$. To the right of the plug let the pressure p be maintained by the piston D. Initially, let the piston D be in contact with the plug E; and as the piston C moves up to the plug, so forcing a gram of the gas through it, let piston D move towards the right. Let the gram of gas have the volume v after being forced through the plug, its volume before being forced through having the value $(v - dv)$. Then, work done *on* gas by piston $C = (p + dp)(v - dv)$, while work done *by* gas on piston $D = pv$. Therefore, **nett work done on gas during operation** $= (p + dp)(v - dv) - pv = vdp - pdv$, when $dp \times dv$ is neglected.

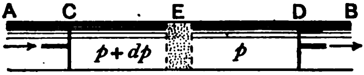

FIG. 2.

No heat enters the gas from outside or leaves the gas through the walls of the cylinder. Therefore, **the net work done on the gas must be equivalent to the increase in the internal energy of the gas.**

Let the temperature of the gas be θ before it is forced through the plug, and $\theta + d\theta$ afterwards; and let the initial and final conditions of the gas correspond to the points A and B (Fig. 3) of the pv diagram. The operation of forcing the gas through the plug is *irreversible*; that is, the gas cannot be caused to pass back again through the plug from the pressure p to the pressure $p + dp$. But the internal energy of the gas at B has the same value whether it has reached that point by an irreversible or by a reversible path. Therefore, the increase in the internal energy of the gas between A and B is equal to the net energy gained by the gas in reaching B by the path A C B, where A C is an isothermal expansion at temperature θ, corresponding to a fall of pressure dp; and C B is an expansion at constant pressure due to a rise of temperature $d\theta$.

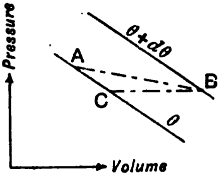

FIG. 3.

During the isothermal expansion, heat gained by gas $= \frac{\theta}{J}\frac{\partial v}{\partial \theta}dp$.

During the constant pressure expansion, heat gained by gas $= s_p d\theta$, where s_p denotes the specific heat of the gas at constant pressure.

External work done by gas during both expansions $= pdv$.

$\therefore$ Net increase in internal energy (measured in ergs)

$$= \theta\frac{\partial v}{\partial \theta}dp + Js_p d\theta - pdv$$

$$\therefore\ vdp - pdv = \theta\frac{\partial v}{\partial \theta}dp + Js_p d\theta - pdv.$$

$$\therefore\ vdp = \theta\frac{\partial v}{\partial \theta}dp + Js_p d\theta,$$

and

$$\frac{d\theta}{dp} = \frac{1}{Js_p}\left\{v - \theta\frac{\partial v}{\partial \theta}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Here, $\frac{d\theta}{dp}$ = heating effect per unit fall of pressure.

Application to perfect gas. Here (p. 483)

$$v - \theta\frac{\partial v}{\partial \theta} = v - \theta\frac{R}{p} = v - \frac{pv}{p} = 0$$

$\therefore$ a perfect gas is neither heated nor cooled by being forced through a porous plug.

Application to water. The value of $\frac{\partial v}{\partial \theta}$ for water can be found from the table on p. 470. For ordinary temperatures, the right-hand side of (*a*) is positive, so that if water is forced under pressure through a porous plug (or through the walls of a porous vessel) the temperature is raised. Notice that in $\frac{\partial \theta}{\partial p}$, pressure is measured in dynes per sq. cm. An atmosphere is nearly equal to 10^6 dynes per sq. cm., so that to determine the rise of pressure per atmosphere fall of pressure, the right-hand side of (*a*) must be multiplied by 10^6.

To determine the absolute zero of temperature. Lord Kelvin found that air and carbon dioxide are cooled by being forced through a porous plug, while hydrogen is heated. In all cases the effect varies with the temperature at which the experiment is conducted (pp. 385-386), but the absolute zero of temperature can be determined by using the mean value of the heating or cooling effect over the range 0° to 100° C. Between these temperatures let the mean heating effect, per atmosphere fall of pressure, be denoted by K, which is a quantity having a positive value for hydrogen, and negative value for air and carbon dioxide. In equation (*a*) writing $10^6\frac{d\theta}{dp} = K$, we find that

$$\theta dv = \left(v - \frac{s_p J K}{10^6}\right)d\theta = (v - k)d\theta.$$

if

$$\frac{s_p J K}{10^6} = k.$$

$$\therefore \frac{dv}{v - k} = \frac{d\theta}{\theta}.$$

Integrating the right-hand side of this equation between θ_0, the absolute temperature of melting ice, and $\theta_0 + 100$; and integrating the left-hand side between the corresponding values v_0 and v_{100} for the volume of a gram of the gas, we find that

$$\int_{\theta_0}^{\theta_0+100} \frac{d\theta}{\theta} = \int_{v_0}^{v_{100}} \frac{dv}{v - k}$$

$$\therefore \Big[\log \theta\Big]_{\theta_0}^{\theta_0+100} = \Big[\log (v - k)\Big]_{v_0}^{v_{100}}$$

$$\therefore \frac{\theta + 100}{\theta_0} = \frac{v_{100} - k}{v_0 - k}$$

$$\therefore 1 + \frac{100}{\theta_0} = 1 + \frac{v_{100} - v_0}{v_0 - k}.$$

Now, on a gas thermometer $pv = \mathrm{R\,T}$, where R and T vary slightly with the gas used, T is the absolute temperature as determined by the gas thermometer in which the gas in question is employed. Then

$$v_{100} = \frac{\mathrm{R}}{p}(\mathrm{T}_0 + 100), \text{ while } v_0 = \frac{\mathrm{R}}{p}(\mathrm{T}_0)$$

$$\therefore \frac{100}{\theta_0} = \frac{\frac{\mathrm{R}}{p}100}{\frac{\mathrm{R\,T}_0}{p} - k} = \frac{100\,\mathrm{R}}{\mathrm{R\,T}_0 - pk}$$

$$\theta_0 - \mathrm{T}_0 = -\frac{pk}{\mathrm{R}}.$$

Here, θ_0 denotes the temperature of melting ice, measured on the absolute dynamical scale; T_0 is the absolute temperature of melting ice measured by the given constant pressure gas thermometer, and is equal to the reciprocal of the coefficient of expansion of the gas at constant pressure. R is a constant found by multiplying the pressure by the volume of a gram of the gas at 0° C., and dividing the result by the absolute temperature of melting ice, measured on a thermometer containing the given gas. Finally, k is determined from the porous plug experiment.

It is found that, using air for the gas thermometer and applying the above correction, $\theta_0 = 273{\cdot}14$. Using hydrogen, the value of $\theta_0 = 273{\cdot}00$. Using carbon dioxide, $\theta_0 = 273{\cdot}04$, while T_0, the absolute temperature of melting ice measured on the constant pressure carbon dioxide thermometer, $= 267{\cdot}24$.

(50) The internal energy of a perfect gas is restricted to the kinetic energy of its molecules and atoms (pp. 301–302). When a perfect gas expands adiabatically, the external work performed is equal to the kinetic energy lost by the gas molecules, and this loss of energy entails a fall of temperature from (say) T_1 to T_2. If the same gas had been *cooled at constant volume* from T_1 to T_2, the molecules of the gas would have lost the same amount of kinetic energy; therefore if the mass of the gas is m, and its specific heat at constant volume is σ_v, the heat which disappears in either case is equal to $m\sigma_v(\mathrm{T}_1 - \mathrm{T}_2)$. Hence work done during adiabatic expansion $= \mathrm{J}m\sigma_v(\mathrm{T}_1 - \mathrm{T}_2)$.

From equation near top of p. 301, $\mathrm{J} = \mathrm{R}/(\sigma_p - \sigma_v)$; therefore work done during adiabatic expansion

$$= m\mathrm{R}.\ \frac{\sigma_v}{\sigma_p - \sigma_v}(\mathrm{T}_1 - \mathrm{T}_2) = \frac{m\mathrm{R}(\mathrm{T}_1 - \mathrm{T}_2)}{\gamma - 1}.$$

Now, from p. 300, RT_1 = product of pressure and volume of *one gram* of the gas at temperature T_1. Therefore $m\mathrm{RT}_1$ = product of pressure p_1 and volume v_1 of m grams of the gas at temperature T_1; and mRT_2 = product of pressure p_2 and volume v_2 of the same m grams of gas at temperature T_2. Hence work performed = $(p_1v_1 - p_2v_2)/(\gamma - 1)$.

If the gas expands to infinity, all of the kinetic energy possessed by its molecules is used up in doing external work, and therefore the temperature falls to zero (absolute); in this case $T_2 = 0$, and $mRT_2 = p_2v_2 = 0$, so that the work done during expansion = $p_1v_1/(\gamma - 1)$. Thus the energy possessed by the molecules comprised in a volume v_1 of gas at pressure p_1 is equal to $p_1v_1/(\gamma - 1)$; this is called the *intrinsic energy* of the gas under the given conditions.

Example.—To find the intrinsic energy of 1 gram of hydrogen at 0° C. under a pressure of 760 mm. of mercury.

A pressure of 760 mm. of mercury = 10^6 dynes per sq. cm. nearly. Under this pressure 1 gram of hydrogen will have a volume of 11,160 c.c. (p. 301). Also $\gamma = 1{\cdot}42$ (p. 302). Thus, intrinsic energy

$$= \frac{10^6 \times 1{\cdot}11 \times 10^4}{1{\cdot}42 - 1} = \frac{1{\cdot}11}{0{\cdot}42} \times 10^{10} = 2{\cdot}64 \times 10^{10} \text{ ergs.}$$

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(*Names of persons are printed in italics.*)

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